GEORGIA INSTITUTE OF TECHNOLOGY — OFFICE OF CONTRACT ADMINISTRATION

PROJECT ADMINISTRATION DATA SHEET

[X] ORIGINAL [ ] REVISION NO. _____

Project No. A-60-614 (R6042-0A0) GTRC/~~GIT~~ DATE 10 /10 /85

Project Director: R. A. Karam School/~~Lab~~ NRC

Sponsor: Kleen-Tex, Inc.

Type Agreement: Standard Research Agreement dated 09/26/85.

Award Period: From 10/01/85 To ~~03/31/86~~ 9-30-86 (Performance) 03/31/86 (Reports)

Sponsor Amount:	This Change	Total to Date
Estimated:	$	$ 18,137
Funded:	$	$ 18,137

Cost Sharing Amount: $ N/A Cost Sharing No: N/A

Title: Characterization of Natural Gas, Oil and Coal Deposits

ADMINISTRATIVE DATA OCA Contact John Schonk X 4820

1) Sponsor Technical Contact:

Kleen-Tex, Inc.
P.O. Box KTI
Le Grange, GA 30241

2) Sponsor Admin/Contractual Matters:

Ralph Howard
Kleen-Tex, Inc.
P.O. Box KTI
Le Grange, GA 30241

Defense Priority Rating: N/A Military Security Classification: N/A
(or) Company/Industrial Proprietary: N/A

RESTRICTIONS

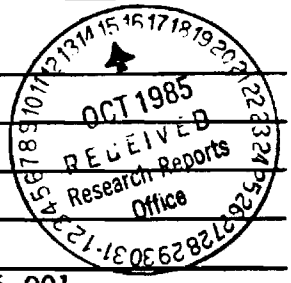
See Attached N/A Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval – Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of $500 or 125% of approved proposal budget category.

Equipment: Title vests with sponsor.

COMMENTS:

An advance payment of $4,500 has been received.



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FORM OCA 65:285

GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date 10/28/86

Project No. A-60-614 School/~~Lab~~ NRC

Includes Subproject No.(s) N/A

Project Director(s) R. A. Karam GTRC /~~XGH~~

Sponsor Kleen-Tex, Inc.

Title Characterization of Natural Gas, Oil and Coal Deposits

Effective Completion Date: 9/30/86 (Performance) 10/10/86 (Reports)

Grant/Contract Closeout Actions Remaining:

- [ ] None
- [x] Final Invoice or Final Fiscal Report
- [ ] Closing Documents
- [ ] Final Report of Inventions
- [ ] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other

Continues Project No. Continued by Project No.

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FORM OCA 69.285

A 60-614

Georgia Institute of Technology
Neely Nuclear Research Center
Atlanta, Georgia 30332
(404) 894-3600

GEORGIA TECH 1885-1985

DESIGNING TOMORROW TODAY

December 3, 1985

Mr. Ralph W. Howard, Jr., President
Kleen-Tex Inc.
P.O. Box KTI
LaGrange, Georgia 30241-2367

Dear Ralph:

This is a progress report to date on the project "Characterization of Natural Gas, Oil and Coal Deposits with Regard to Distribution, Depth, and Trace Elements Content." The report is organized as follows:

I. Natural Gas and Oil Wells and Coal Beds Characterization

I.1 Geographical Distribution
I.2 Relationship to Faults
I.3 Relationship to Permeability
I.4 Relationship to Plate Tectonics
I.5 Illustrative Examples

II. Trace Elements in Hydrocarbon Fuels

II.1 Trace Elements in Coal
II.2 Trace Elements in Oil
II.3 Trace Elements in Natural Gas
II.4 Additional Data about Trace Elements and References

The material which follows was prepared by Dr.Wampler, J.N. Eto and Musa Yavuz.

I expect that we will spend some time assessing this data and will report to you our findings.

If you have any questions, please let me know.

Sincerely yours,

R.A. Karam
Director

RAK:jlr

I. NATURAL GAS AND OIL WELLS AND COAL BEDS CHARACTERIZATION

During October we have been gathering information on coal beds and on natural gas and oil pools, for the purpose of quantitative characterization of these fuels with respect to geographic distribution and relationships to faults, to permeability, and to plate tectonics. Because of the great volume of such information available for the entire world, most of our effort has been focused on one state, Pennsylvania, which has been a major producer of coal, oil, and gas. Even in this one state, a complete listing of all known coal beds and oil and gas pools would be a formidable task. Consequently, we have obtained maps, tables, and text that provide general information about the distribution and character of these fuels in Pennsylvania and have supplemented this general information with specific examples of sequences of coal-bearing rocks and of oil and gas pools in particular localities.

Following is a brief summary of the information obtained during October, outlined in accordance with the items in the original proposal.

I.1 Geographical Distribution

Coal is broadly distributed in Pennsylvania, from the anthracite fields in the Appalachian Ridge and Valley Province in eastern Pennsylvania to the bituminous fields that involve most of the Appalachian Plateau of western Pennsylvania. In the major bituminous fields there are dozens of individual coal seams, variable in thickness but typically reaching maximum thicknesses of three to six feet, within a sequence of sedimentary rocks that is several thousand feet thick. The coals of Pennsylvania are limited to the two uppermost Paleozoic rock systems, the Pennsylvanian and Permian systems.

Petroleum and especially natural gas fields are also broadly distributed in Pennsylvania, and although there is considerable overlap of these fields with the coal fields on a map of the state, the actual distribution of gas and petroleum is distinctly different from the distribution of coal, a fact that is particularly evident when the third dimension is considered. For example, there is a northeast-southwest trending belt of gas reservoirs that runs under the eastern portion of the main bituminous coal field. The gas pools are generally in rocks much deeper (and much older) than the coal beds, and these gas fields extend beyond the main bituminous field to the northeast where there is little coal.

I.2 Relationship to Faults

Faults are common in both coal fields and oil and gas fields. Generally, the faults observed in bituminous coal fields are minor features that have offset the sedimentary rock layers,

including the coal seams, as a consequence of minor tectonic movements generally long after the rocks were deposited. The anthracite fields of eastern Pennsylvania are, however, in a region where major tectonic movement caused severe folding of the rock layers and the development of major thrust faults.

Many oil and gas pools have formed as a direct consequence of faulting, because the offset of a permeable formation due to faulting often forms a structural trap for the fluid hydrocarbons. Faults may also be present in fields where the trapping is due to another characteristic of the rock formations (e.g., structural doming of rock layers, or a change in permeability). In general, the faults associated with oil and gas fields are minor features, which in some cases (e.g., "growth faults") formed contemporaneously with the deposition of sediments and in other cases have formed as a result of tectonic movements long after the sedimentation had ceased. In the western U.S., an important area of petroleum production is associated with major thrust faults, but in Pennsylvania the important gas and oil fields are well to the west of the main Appalachian thrust faults.

I.3 Relationship to Permeability

Natural gas and oil pools are formed within permeable rocks that are capped by impermeable formations, which prevent the fluid fuels from moving (further) upward. There is no such relationship in the occurrence of coal, since coal is a solid with no tendency to migrate through permeable rocks. Minor coal beds are commonly observed within permeable sandstones and conglomerates, but the significant coal seams of Pennsylvania are typically sandwiched between clay-rich shale beds, which are relatively impermeable.

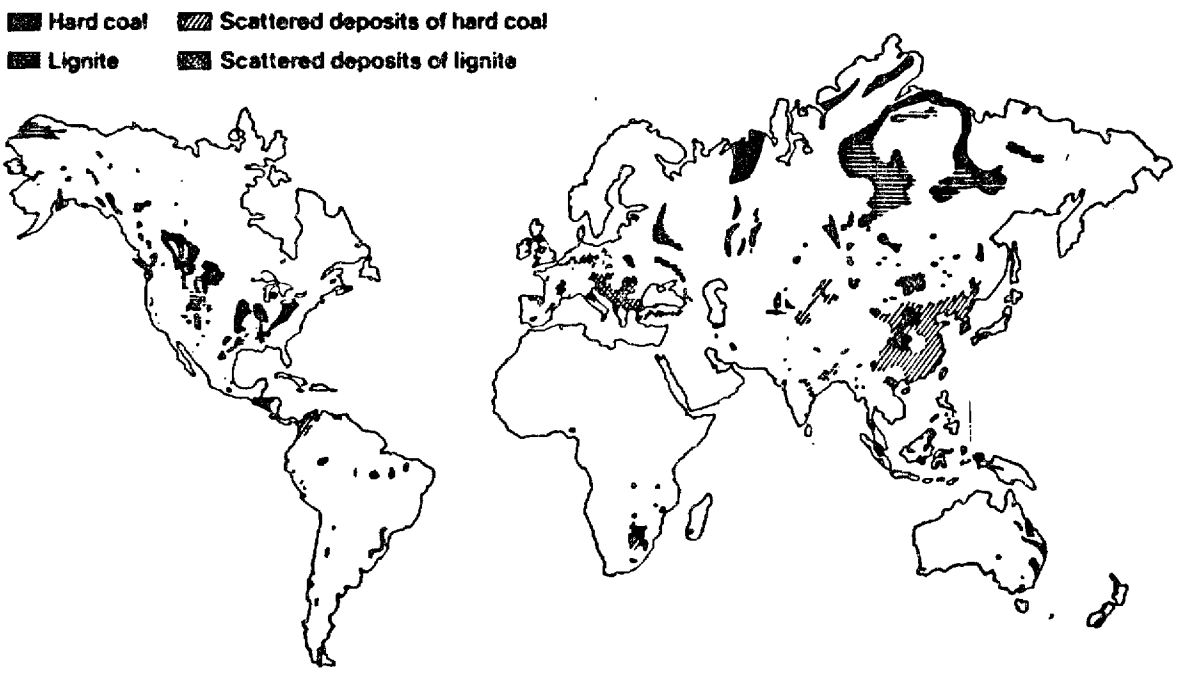
I.4 Relationship to Plate Tectonics

Pennsylvania is far from the present boundaries of the North American tectonic plate, but the Paleozoic rocks that contain the coal, oil, and gas deposits were formed in proximity to a continental margin (the eastern margin of the Paleozoic precursor of North America) that was tectonically active throughout much of the time that these rocks were forming. Hence, there is a very important association between the rocks that contain the fuels and the plate-tectonic activity that occurred during and after the deposition of these sedimentary rocks.

It should be made clear that the faults that are common within the coal, oil, and gas fields are generally relatively small faults (that is, faults of relatively small displacement, which have quite a limited extent both laterally and vertically) that affect only the brittle upper part of the earth's crust. Such faults are much different in character than the major fault zones that are actually the boundaries between tectonic plates (e.g., the San Andreas fault zone). The relative displacement

along plate boundaries may be hundreds of kilometers, and the zone of relative motion extends downward through the lithosphere. The character of the deformation in these great fault zones gradually changes in character from brittle fracture in the upper crust to flowage at the base of the lithosphere. (The base of the lithosphere is not sharply defined but is generally between fifty and one hundred kilometers depth.)

I.5 Illustrative Examples and Maps of Oil, Coal, and Natural Gas Follow.



Map showing world coal resources. Note that on this scale none of the great complexity of the coal fields of Pennsylvania could be shown.

Source: IEA Coal Research

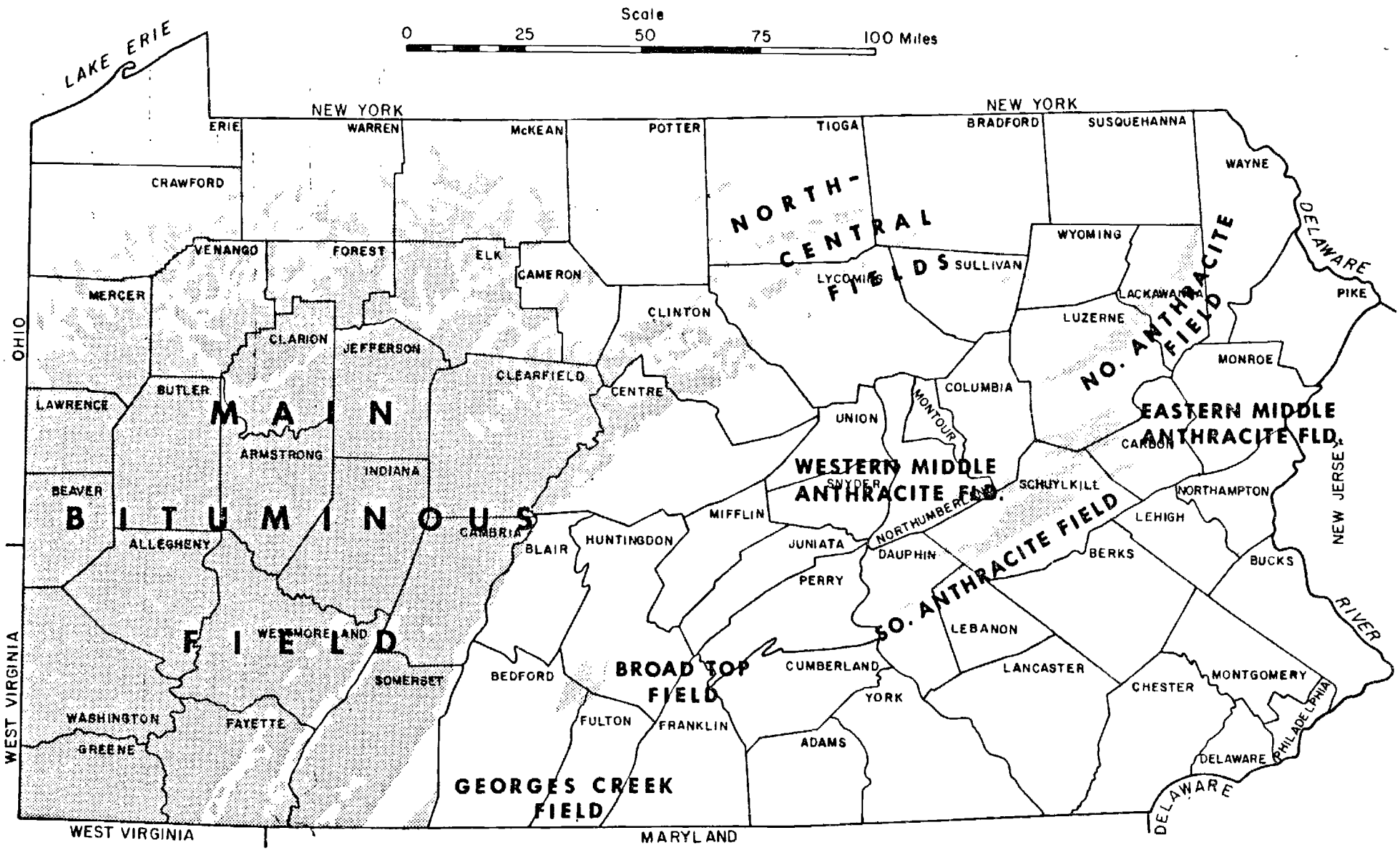
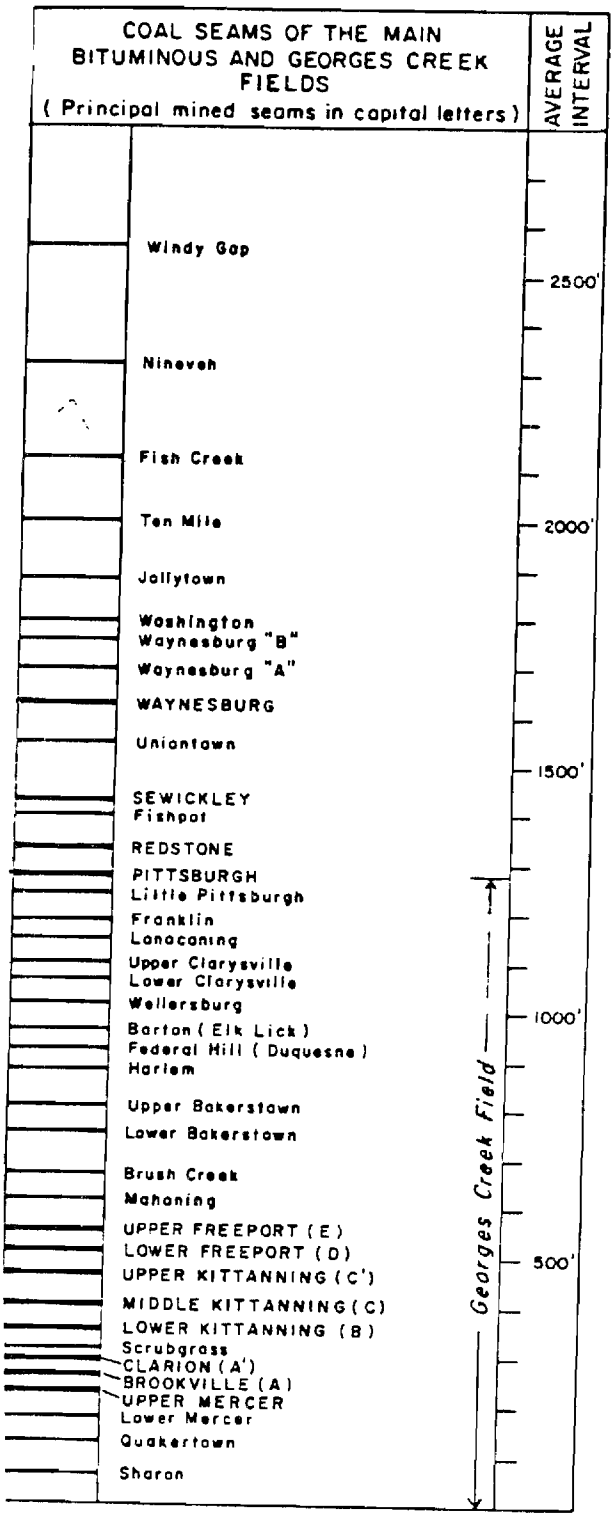


Figure 1. Coal fields of Pennsylvania.

Map showing the coal fields of Pennsylvania. Not shown in this view is the vertical distribution of coal beds nor the stratigraphical positions of the coal beds.

Source: 1974 Keystone Coal Industry Manual



. Coal seams of the Main Bituminous and Georges Creek Coal Fields.

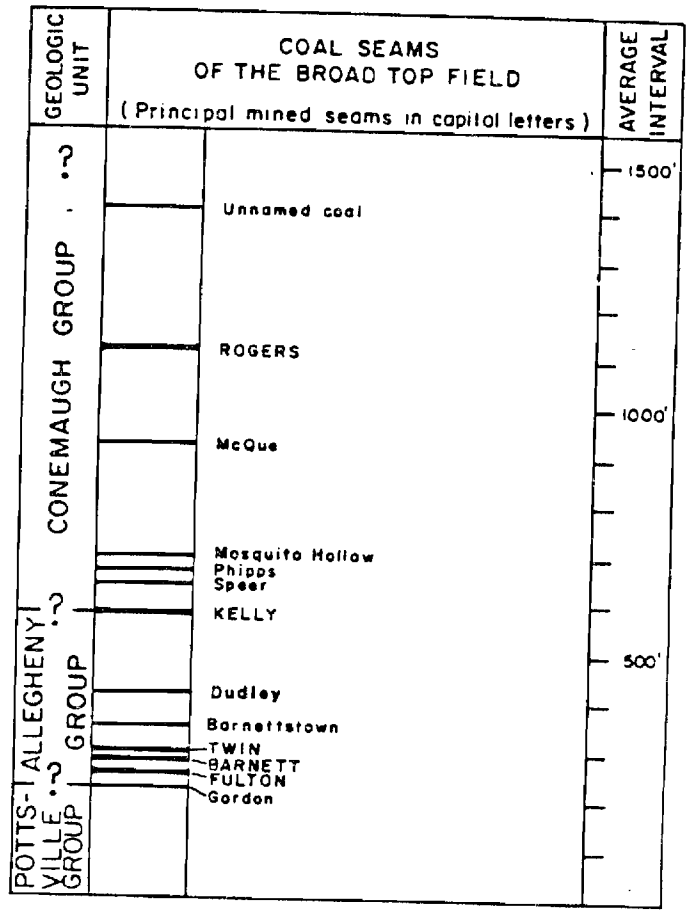


Figure 5. Coal seams of the Broad Top Coal Field.

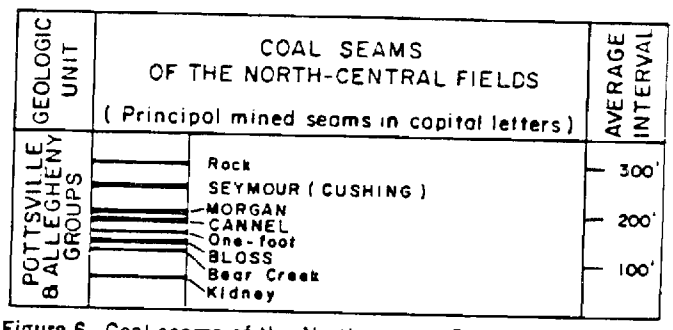
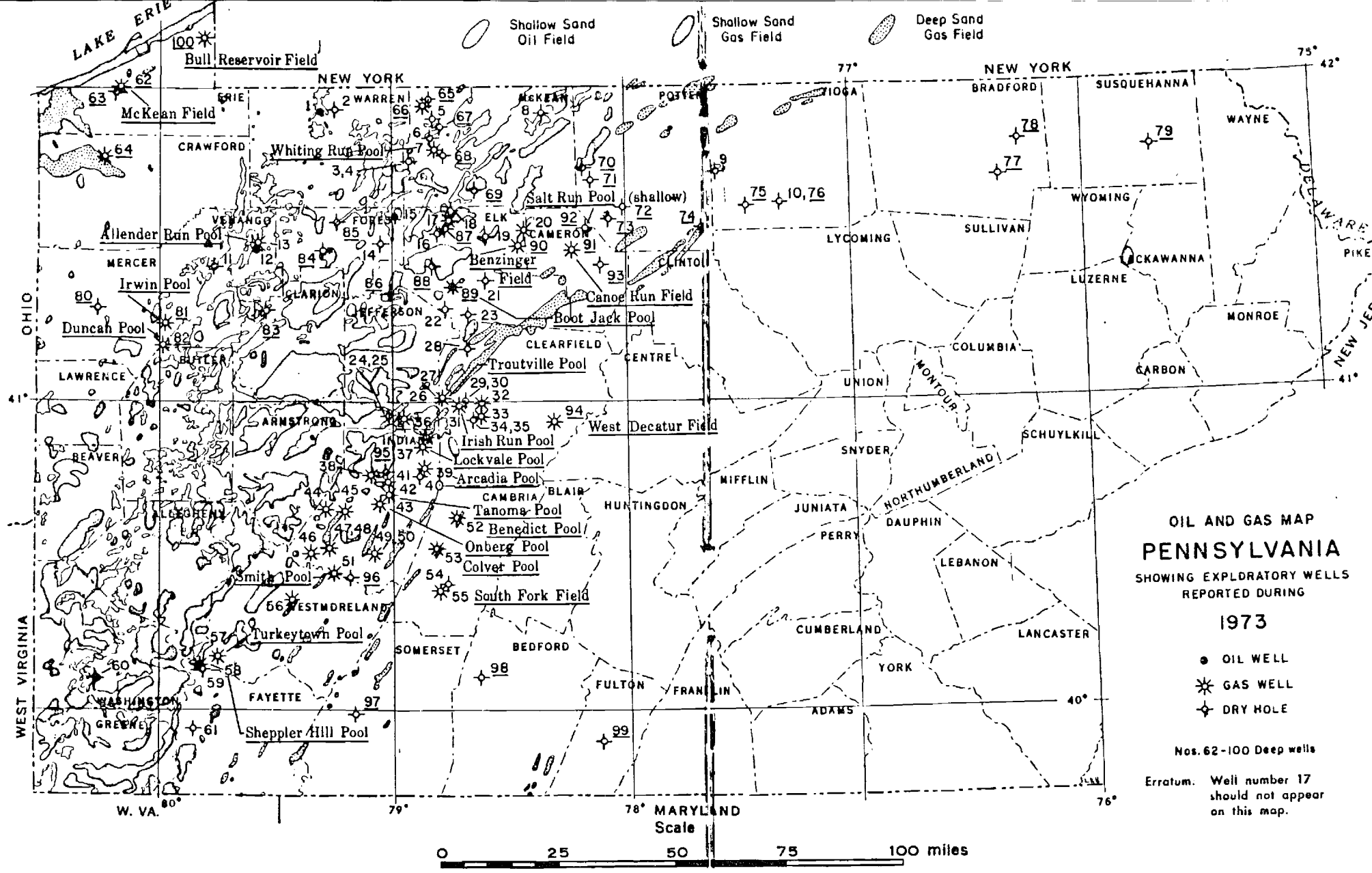


Figure 6. Coal seams of the North-central Coal Fields.

. Vertical distribution of coal seams in the major bituminous-coal fields of Pennsylvania. In addition to the information shown about the distances between coal seams, it is also significant that the coal beds are limited to the upper Paleozoic rocks of Pennsylvania, rocks formed during the Mississippian, Pennsylvanian, and Permian Periods.

Source: 1974 Keystone Coal Industry Manual



Map showing the oil and gas fields of Pennsylvania. It is noteworthy that the oil pools occur only in shallow sands. Natural gas occurs in shallow sands but also in deeper (and much older) sands.

Source: Pennsylvania Topographic and Geological Survey Progress Report No. 186-187.

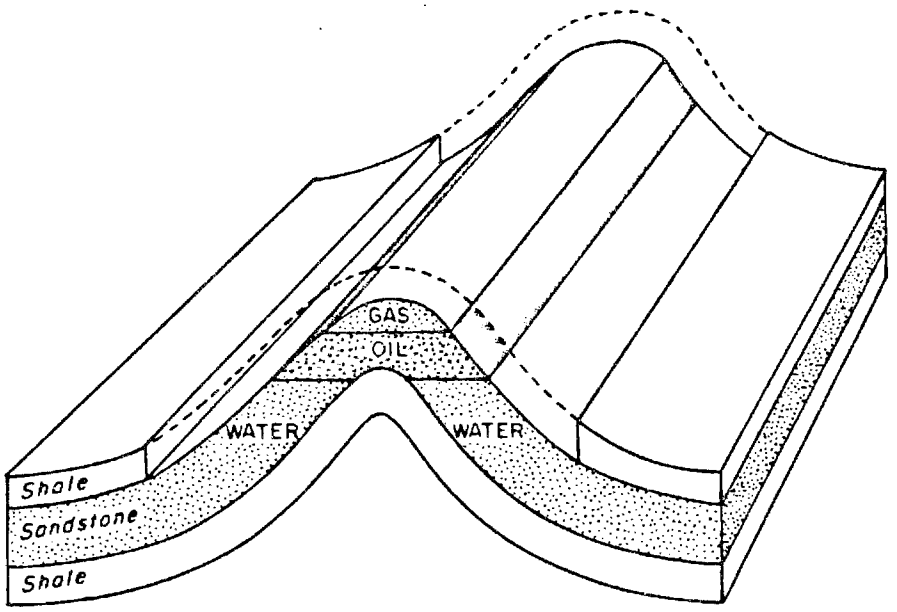


Figure 7. Entrapment of oil and gas in an anticline.

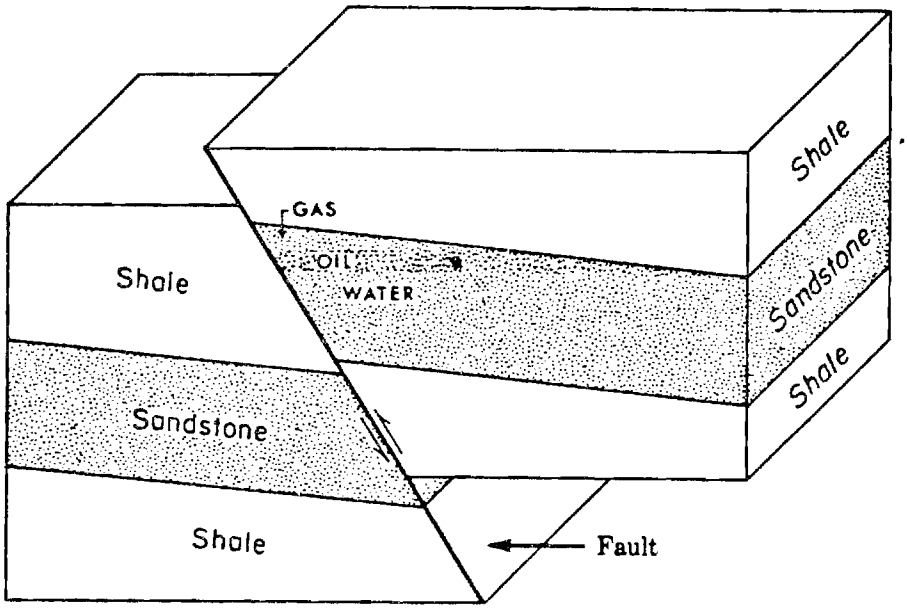


Figure 8. Entrapment of oil and gas by faulting.

Schematic diagram showing two of the most common structural traps for oil and gas. In the upper figure, fluid fuels are within an anticlinal portion of a permeable sandstone, prevented from moving further upward by an impermeable shale that overlies the sandstone. In the lower figure the fluids are trapped in a portion of a sandstone where it abuts impermeable shale as a consequence of offset by faulting.

Source: Introduction to Sedimentology, by R. C. Selley

Most of the structural traps in Pennsylvania occur along a northeast trending belt extending from Fayette County on the southwest to Potter and Tioga Counties on the northeast. This belt is shown on the Oil and Gas Fields Map (Center fold map) by a scattering of fields colored dark green. These fields have produced gas from a rock formation of Early Devonian age called the Oriskany sandstone. The dark-green fields in this structural belt, and also in the northwest corner of the State, are called deep sand gas fields because they lie several thousand feet below the fields colored pink and light green. The Oriskany sandstone is 4,500 to 5,000 feet deep in Potter and Tioga Counties and becomes deeper to the southwest; in Fayette County it is 8,000 to 8,500 feet deep.

Figure 9 is a section through the anticline containing the Leidy gas field, Clinton County. The location of the section is shown by line A-B in the inset map. Near the surface, as can be seen by the arching of the sandstone bed, the anticline is a smooth, gentle fold, but 4,000 to 6,000 feet below sea level the structure is more complex. Here the Oriskany sandstone and an overlying formation, the Tully limestone, are both folded and faulted. In the Oriskany sandstone are two gas pools separated by faults, the Leidy pool and the Tamarack pool. Because of the

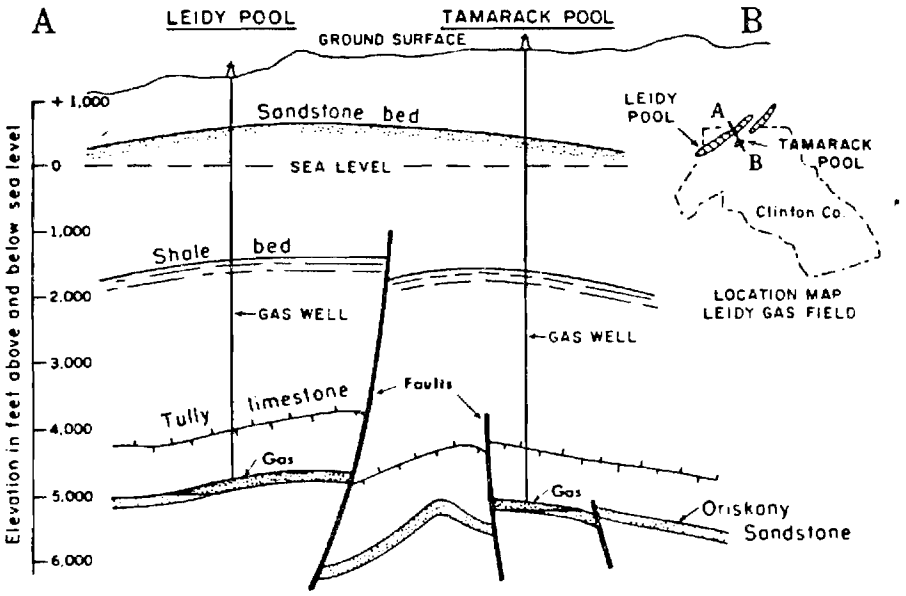


Figure 9. Cross section of Leidy gas field. Entrapment of gas in folded and faulted anticline. Note that faults in Oriskany and Tully disappear before reaching surface.

Cross section showing an example of the role of faults in trapping fluid fuels, in this case natural gas. Offsets on two faults have caused gas to become trapped in portions of the permeable Oriskany sandstone. These gas pools are in rocks considerably deeper (and thus older) than the rocks that contain coal and the rocks that contain oil in Pennsylvania.

Source: Pennsylvania Topographic and Geologic Survey, Educational Series No. 1-8.

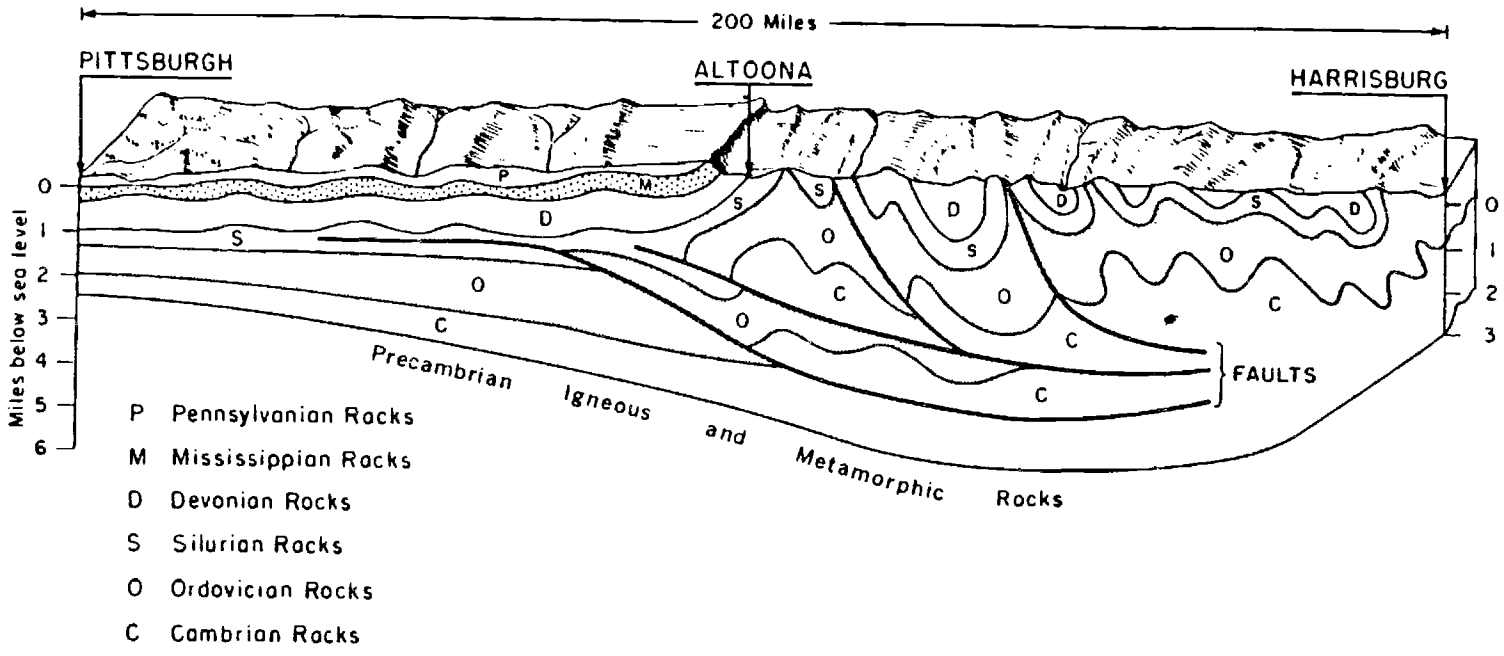


Figure 6. Cross section from Pittsburgh to Harrisburg showing folding and faulting of subsurface rocks.

Cross section showing the deformation of rocks in Pennsylvania caused by convergence of tectonic plates late in the Paleozoic Era. The faults shown are major thrust faults produced by the convergence. Not shown are many smaller faults of such limited extent that they could not be shown on a diagram of this scale.

Source: Pennsylvania Topographic and Geologic Survey, Educational Series No. 1-8.

II. CHARACTERIZATION OF TRACE ELEMENTS IN HYDROCARBON FUELS

In this study we seek to tabulate quantitatively all trace elements that are found in coal, oil and natural gas. A large database exists for coal and oil. Trace elements in natural gas, however, have not been reported to any extent.

II.1 Trace Elements in Coal

Studies of trace elements in coals have been conducted for more than 100 years [1]. However, the application of modern methods is attributed to Goldschmidt, who first applied instrumental techniques to the problem in the mid-1930's. Many trace elements are present in coals; in all, about 40 such elements have been identified. Other elements may also be present. Several excellent studies have been conducted in recent years. Zubovic and his co-workers at USGS have studied trace elements in coals on a regional basis [2], [3], [4], [5], [6]. These investigations included coals from the Appalachian, eastern interior, western and southwestern interior, and Northern Great Plains regions. Emission spectroscopic analyses were used to determine the concentrations of 15 minor elements in these coals. The average trace element content appears in Table 6.

II.2 Trace Elements in Oils

Although petroleum consists of predominantly hydrocarbons, most petroleums contain measurable quantities of many metals. Nickel and Vanadium are commonly the most abundant metals, but Fe, Zn, Cr, Cu, Mn, Co, and others are almost always in concentrations from less than 1 ng/g to more than 100 µg/g. The nature of these metals and their abundances in crude oil can give information on the origin, migration, and maturation of petroleum as well as providing a basis for regional geochemical prospecting.

A total of 29 elements was determined in oils representing the various producing formations of the Iraqi oil fields by Al-Shahristani and Al-Alvia [1]. The elements determined include: Al, Ar, As, Au, Br, Ca, Cl, Co, Cr, Cu, Eu, Fe, Ga, Hg, K, La, Mn, Mo, Na, Ni, Re, S, Sb, Sc, Se, Sm, V, W, and Zn. Concentrations reported for different elements from different parts of the world differ significantly. Data from analyses of oil samples from different wells in the same field indicate that metals in crude oil are not uniformly distributed in each oil field.

As an example, Table 7 shows concentration data for four crude oils as reported by Filby and Shah [2] and Hitchon et al. [3].

A crude oil classification scheme described by Hyder [4] allows association of a metal with a particular type of hydrocarbon to be relieved by the distribution patterns of metal content in oil classes. The author has concluded that Vanadium content seems to be related to oil classes. Nickel, as Vanadium, also shows a general increase with the increase in oil class number. Ga, Cr, and Mo also show this tendency but to a lesser degree than V and Ni; Uranium seems to be independent of oil class. For other metals there is no clear pattern.

Here, the attention is also focused on Potassium-40, Rubidium-87 and their daughter products as mentioned at the previous section. The information related to concentrations of Rubidium, Strontium, Potassium and Calcium is as follows:

Rubidium (Rb): Rb has been detected in nine of 88 crude oil samples from Alberta, [3]. Tne average concentration: 0.015 ppm.

Strontium (Sr): In the ash of crude oils from the western U.S., it has been determined that Sr concentrations are within the range 0.01-0.1%, [4].

Potassium (K): The concentration level of Potassium in the crude oil from Libya was reported to be 4.9 µg/g, [2]. Hyder, [4], has found potassium in the refinery residues only.

Calcium (Ca): Hyder, [4], has reported that out of 120 samples of crude oils from the western half of the U.S. most had Ca content within 0.5-5% in the ash.

II.3 Trace Elements in Natural Gas

Even though there have been a number of studies for trace elements in coal and in oil, there has been no sufficient research for trace elements in natural gas.

The composition of purified natural gas depends upon its origin. It consists predominantly of methane with varying concentrations of ethane, nitrogen and carbon dioxide. Small quantities of higher saturated hydrocarbons are always present. The composition of natural gas appears in Table 8.

Normally, natural gas contains minute quantities of radon and in isolated cases, traces of mercury. The concentrations in which they occur are n the order of 10^{-13} µg/m^3 and 2×10^{-5} g/m^3 respectively [8].

In the reference [9], it is emphasized that trace elements in natural gas are V, Ni, Hg and N_2 in regional patterns. However, there is no information available about quantitative values of those elements.

TABLE 1: AVERAGE TRACE-ELEMENTS CONTENTS FOR COALS FROM VARIOUS REGIONS OF THE U.S.[a]

Element	SWI[b]	EI[c]	NGP[d]	APP[e]
B	33	96	116	25
Be	1.1	2.5	1.5	2.5
Co	4.6	3.8	2.7	5.1
Cr	13	20	7	13
Cu	11	11	15	15
Ga	2.0	4.1	5.5	4.9
Ge	5.9	13	1.6	5.8
La	6.5	5.1	9.5	9.4
Mo	3.1	4.3	1.7	3.5
Ni	14	15	7.2	14
Sn	1.3	1.5	0.9	0.4
Ti	250	450	591	350
V	18	35	16	21
Y	7.4	7.7	13	14
Zn	108	44	59	7.6

[a]ppm.
[b]SWI = Forty-eight coals from Western and Southwestern Interior Region.
[c]EI = Eastern Interior Region, 53 coals.
[d]NGP = Northern Great Plains Region, 51 samples.
[e]APP = Seventy-three coals from Appalachian region.

SOURCE: References [2], [3], [4], [5], [6]

A group at Penn State University, headed by O'Gorman and Walker, considered the trace-element content of coals by ASTM rank [7[, [8]. A total of 57 samples ranging from lignite to anthracite was analyzed by atomic absorption spectrometry and emission spectroscopy. The average trace-element concentration in the ashes obtained from the various coals are given in Table 2.

TABLE 2: AVERAGE TRACE-ELEMENT CONTENTS OF THE ASH FROM U.S. COALS OF VARIOUS RANK[a]

Element	Anth[b]	LVB[c]	MVB[d]	HVB[e]	L(SB)[f]
Ag	<1	<1	<1	<1	<1
B	90	123	218	770	1010
Ba	866	740	896	1253	5027
Be	9	16	13	17	6
Co	81	172	105	64	45
Cr	304	221	169	193	54
Cu	405	379	313	293	655
Ga	42	41		40	23
Ge	<20	<20			
La	142	110	83	111	62
Mn	270	280	1432	120	688
Ni	220	141	263	154	129
Pb	81	89	96	183	60
Sc	61	50	56	32	18
Sn	962	92	75	171	156
Sr	177	818	668	1987	4660
V	248	278	390	249	125
Y	106	152	151	102	51
Yb	8	10	9	10	4
Zn		231	195	310	
Zr	688	458	326	411	245

[a]ppm.
[b]Anth = Anthracite.
[c]LVB = low-volatile bituminous.
[d]MVB = medium-volatile bituminous.
[e]HVB = high-volatile bituminous.
[f]L(SB) = lignite (subbituminous)

SOURCE: References [7], [8]

Work conducted at USGS resulted in the identification of many of the elements present in Illinois coals [9], []0]. The trace elements in 80 Illinois Basin coals were analyzed by neutron activation analyses, emission spectroscopy, atomic absorption spectroscopy, X-ray spectroscopy, and ion-selective electrode. The averages for the elements found in these coals are reported in Table 3.

TABLE 3: TRACE-ELEMENT CONTENTS OF EIGHTY-TWO COALS FROM THE ILLINOIS BASIN[a]

Element	Average	Element	Average
As	14.9	K (%)	0.16
Al (%)	1.22	Mn	53.2
B	113.8	Mg (%)	0.05
Be	1.7	Mo	8.0
Br	15.3	Na (%)	0.05
Ca (%)	0.74	Ni	22.4
Cd	2.9	P	62.8
Cl (%)	0.15	Pb	39.8
Co	9.2	Sb	1.4
Cr	14.1	Se	2.0
Cu	14.1	Si (%)	2.4
F	59.3	Sn	4.6
Fe (%)	2.06	Ti (%)	0.06
Ga	3.0	V	33.1
Ge	7.5	Zn	313.0
Hg	0.2	Zr	72.1

[a]All values in ppm unless otherwise indicated.

SOURCE: References [9], [10]

In addition to these efforts, there have been several other excellent studies and/or reviews about trace elements in coals [2], [4], [11], [12], [13], [14], [15], [16], [17]. Information from these sources and those mentioned earlier was compiled into listings of the ranges of concentration of the various trace elements found in American coals and ashes. These lists appear in Table 4 and Table 5.

TABLE 4: RANGE OF TRACE ELEMENTS IN U.S. COALS[a]

Major Elements[b]		Minor Elements	
Element	Range (%)	Element	Range (ppm)
Na	0 - 0.20	Be	0 - 31
Mg	0.1 - 0.25	B	1.2 - 356
Al	0.43 - 3.04	F	10 - 295
Si	0.58 - 6.09	P	5 - 1430
Cl	0 - 0.56	Sc	10 - 100
K	0.02 - 0.43	V	0 - 1281
Ca	0.05 - 2.67	Cr	0 - 610
Ti	0.002 - 0.32	Mn	6 - 181
Fe	0.32 - 4.32	Co	0 - 43
Zn[c]	0 - 0.56	Ni	0.4 - 104
		Cu	1.8 - 185
		Ga	0 - 61
		Ge	0 - 819
		As	0.5 - 106
		Se	0.4 - 8
		Br	4 - 52
		Y	<0.1 - 59
		Zr	8 - 133
		Mo	0 - 73
		Cd	0.1 - 65
		Sn	0 - 51
		Sb	0.2 - 9
		La	0 - 98
		Hg	0.01 - 1.6
		Pb	4 - 218
		U	<10 - 1000

[a]Data by Deul and Annell in references below have been omitted.
[b]Elements present in 0.2% in coals.
[c]Zinc is not normally considered a major element in coals.

SOURCE: References [2], [3], [4], [5], [6], [11], [16], and [17]

TABLE 5: RANGE OF TRACE-ELEMENT CONCENTRATIONS IN ASHES FROM U.S. COALS[a]

Major Elements[b]		Minor Elements	
Element	Range (%)	Element	Range (ppm)
Na	0.71 - 2.72	Li	<20 - 3100
Mg	0. - 2.4	Be	0 - 1100
Al	5.3 - 21.2	B	30 - 6500
Si	9.3 - 28	P	<440 - 3360
K	0.66 - 1.32	Sc	2 - 155
Ca	0.58 - 14	V	6 - 3800
Ti	0.1 - 2.6	Cr	<1 - 1800
Fe	2.09 - 24.4	Mn	30 - 1800
Zn[c]	0. - 1.6	Co	0 - 600
Sr	0.009 - 0.96	Ni	0 - 1200
Ba	0.01 - 1.39	Cu	10 - °0'0
		Ga	0 - 540
		Ge	0 - 1500
		As	21 - 570
		Rb	<91 - 1100
		Y	0 - 620
		Zr	100 - 1450
		Mo	0 - 2900
		Ag	<1 - 84
		Sn	0 - 4250
		Sb	<40 - 230
		La	0 - 820
		Yb	<2 - 23
		W	<10 - 182
		Hg	<70 - 259
		Pb	10 - 1420
		Bi	1 - 900

[a]Data by Deul and Annell in references below have been omitted.
[b]Elements present in >0.7%.
[c]Zinc is not normally considered a major element in coals.

SOURCE: References [2], [3], [4], [5], [6], [7], [8], [11], [15], [16], [18]

TABLE 6: CONCENTRATIONS OF POTASSIUM, CALCIUM, RUBIDIUM, AND STRONTIUM IN SOME U.S. COALS

Potassium Concentration

Area	Conc range (%)	Arithmetic mean (%)	Geometric mean (%)
Illinois Basin	0.04-0.56	0.17	0.16
Eastern U.S.	0.06-0.68	0.25	0.21
Western U.S.	0.01-0.32	0.05	0.03

Calcium Concentration in Some U.S. Coals

Area	Conc range (%)	Arithmetic mean (%)	Geometric mean (%)
Western U.S.	0.44-3.8	1.7	1.5
Eastern U.S.	0.09-2.6	0.47	0.34
Illinois Basin	0.01-2.7	0.67	0.51

Rubidium Concentration in Some U.S. Coals

Area	Conc range (%)	Arithmetic mean (%)	Geometric mean (ppm)
Western U.S.	0.30-29	4.6	2.4
Eastern U.S.	9.0-63	22	19
Illinois Basin	2.0-46	19	17

Strontium Concentration in Some U.S. Coals

Area	Conc range (%)	Arithmetic mean (%)	Geometric mean (ppm)
Western U.S.	93-500	260	220
Eastern U.S.	28-550	130	100
Illinois Basin	10-130	35	30

SOURCE: Reference [19]

Except for a few elements which are thought to be almost exclusively associated with the organic coal components, most of the trace elements in coals are distributed among or within the major mineral constituents [2], [4], [9], and [10].

The attention is focused on some trace elements such as Potassium-40 and Rubidium-87 which are naturally radioactive with very long halflives, approximately 1-50 billion years. Their daughter products are Calcium-40 and Strontium-87, respectively. The information related to concentrations of Potassium, Calcium, Rubidium and Strontium in some U.S. coals is given in Table 6 [19].

TABLE 7: TRACE ELEMENT CONTENTS OF SOME CRUDE OILS BY NEUTRON ACTIVATION ANALYSIS

	Concentration in Crude Oil (ppm)				
Element	California[2]	Libya[2]	Venezuela[2]	Alberta[2]	Alberta[3]
As	0.655	0.077	0.284	0.0024	0.111
Br	0.29	1.33	—	0.072	0.491
Cd	0.004	—	—	—	—
Cl	1.47	1.81	—	25.5	39.3
Co	13.5	0.032	0.178	0.0027	0.054
Cr	0.640	0.0023	0.430	—	0.093
Cu	0.93	0.19	0.21	—	—
Fe	68.9	4.94	4.77	0.696	10.8
Ga	0.30	0.01	—	—	—
Hg	23.1	—	0.027	0.084	0.051
I	—	—	—	1.36	0.719
K	—	4.93	—	—	—
Mn	1.20	0.79	0.21	0.048	0.01
Mo	—	—	7.85	—	—
Na	13.2	13.0	20.3	2.92	3.62
Ni	98.4	49.1	117	0.609	9.38
S	9.90	4694	—	1450	830
Sb	0.056	0.055	0.303	—	—
Sc	0.0009	0.0003	0.004	—	0.0008
Se	0.364	1.10	0.369	0.0094	0.0052
U	—	0.015	—	—	—
V	7.5	8.2	1110	0.682	13.6
Zn	9.76	62.9	0.692	0.670	0.046

[2] Filby and Shah (1975).
[3] Hitchon, Filby, Shah (1975)

Table 7, obtained from Reference [4], shows that the order of abundance of metals in the ash of crude oils, with some exceptions, is similar to that in the crust of the earth. Vanadium and Nickel are the notable exceptions; these metals are the most abundant in the ash of crude oil. Molybdenum also appears to be more abundant in the ash of oil relative to its average content in the crust of the earth.

TABLE 8: COMPOSITION OF NATURAL GASES

Composition % V/V	U.K. North Sea Leman Bank	Holland Groningen	U.S.A. Monroe Louisiana	U.S.A. Amarillo Texas	U.S.A. Ashland Kentucky	+
CH_4	94.7	81.2	94.7	72.9	75.	90
C_2H_6	3.0	2.9	2.8	19	24.	8.4
C_3H_8	0.5	0.4	----	----	----	1.7
C_4H_{10}	0.2	0.1	----	----	----	
CO_2	0.1	0.9	0.2	0.4	----	
N_2	1.3	14.4	2.3	7.7	1.	
He	0.1	0.1	----	----	----	
C_5+	0.2	0.1	----	----	----	

References: [5], [6]

(+) Typical natural gas, from Reference [7]

II.4 ADDITIONAL DATA ABOUT TRACE ELEMENTS AND REFERENCES

TABLE 9: PREFERRED LASL METHODS FOR ELEMENTAL ANALYSES OF COALS AND COAL WASTES [20]

Element	Method	Element	Method
Li	AA, OES	Br	NAA
Be	AA, OES	Rb	NAA, OES
B	OES	Sr	NAA
F	C	Y	OES
Na	NAA	Zr	OES
Mg	NAA, OES	Mo	OES
Al	NAA, OES	Ag	AA
Si	AA, OES, C	Cd	AA
P	AA, C	Sn	OES
S	C	Sb	NAA
Cl	NAA, C	I	NAA
K	NAA, OES	Cs	NAA
Ca	NAA	Ba	NAA
Sc	NAA, OES	La	NAA, OES
Ti	NAA, AA	Ce	NAA
V	NAA, AA, OES	Sm	NAA
Cr	NAA, AA, OES	Eu	NAA, OES
Mn	NAA, AA, OES	Tb	NAA
Fe	NAA, AA	Yb	NAA, OES
Co	NAA, AA, OES	Lu	NAA
Ni	AA, OES	Hf	NAA
Cu	AA, OES	Ta	NAA
Zn	NAA, AA	W	NAA
Ga	NAA, OES	Hg	NAA, AA
Ge	OES	Pb	AA, OES
As	NAA, AA	Th	NAA
Se	NAA	U	NAA

Note: Methods for analyses were: NAA — Neutron Activation Analysis, AA — Atomic Absorption Spectrophotometry, OES — Optical Emission Spectroscopy, and C — Chemical Methods.

TABLE 9 shows the preferred LASL methods for elemental analyses of coal and coal wastes.

TABLE 10: COAL ANALYSIS FOR TRACE ELEMENTS-COMPARISON OF METHODS [21]

	Laboratory Code										
	1	3	6	1	3	2	3	4	5	3	3
	Analytical Method										
Elements Analyzed	SSMS*	SSMS*	SSMS*	OES**	OES**	NAA***	NAA***	NAA***	NAA***	NAA***	AAS
	ppm (by weight)										
Hg	<2	<2	<0.10	NA	NA	<0.2	NA	<0.02	0.03	NA	0.051†
Be	0.4	NA	0.4	<1	<0.1	NA	NA	NA	NA	NA	NA
Cd	6	<1	0.7	<30	<10	NA	<3	<40	NA	NA	NA
As	2	2	0.25	<100	<50	<1	1.4	1.6	NA	<1	NA
V	10	NA	7.7	10	10	7.0	5.5	7	NA	6.0	NA
Mn	20	3	1.9	10	20	7.6	4.8	6.7	NA	5.0	NA
Ni	<40	4	6.0	<10	<20	NA	NA	<20	NA	NA	NA
Sb	0.6	NA	0.04	<30	<10	0.14	0.2	0.4	NA	NA	NA
Cr	<30	7	12	<10	<30	3.4	5.0	4.8	NA	NA	NA
Zn	<100	5	6.6	<100	<50	NA	NA	<100	NA	NA	NA
Cu	10	9	4.5	10	10	NA	NA	<0.4	NA	NA	NA
Pb	<4	4	1.8	<30	<10	NA	NA	NA	NA	NA	NA
Se	<15	<8	0.1	NA	NA	1.0	5.0	2.0	1.5	NA	NA
B	15	5	14	10	7	NA	NA	NA	NA	NA	NA
F	<2	4	60	NA	NA	NA	NA	NA	NA	NA	NA
Li	0.3	NA	2.8	<300	10	NA	NA	NA	NA	NA	NA
Ag	<2	NA	<0.1	<1	<1	NA	NA	<2	NA	NA	NA
Sn	3	NA	0.19	<30	<10	NA	NA	NA	NA	NA	NA
Fe	2,000	2,000	1,800	2,000	3,000	2,400	2,700	3,140	NA	8,000	NA
Sr	100	50	46	<30	NA	160	NA	120	NA	80	NA
Na	600	100	660	300	500	800	870	840	NA	800	NA
K	100	50	200	150	20	NA	2,200	280	NA	100	NA
Ca	10,000	10,000	5,800	8,000	10,000	NA	5,500	7,070	NA	NA	NA
Si	6,000	10,000	10,000	3,000	20,000	NA	NA	NA	NA	NA	NA
Mg	2,000	700	2,000	600	100	2,600	NA	920	NA	1,000	NA
Ba	400	30	110	500	200	NA	220	430	NA	<2.0	NA

*Analysis on sample direct. **DC arc on sample direct. ***Instrumental NAA. †Dissolution followed by flameless AAS.

Note: NAA, neutron activation analysis; SSMS, spark source mass spectrometry; OES, optical emission spectrometry; AAS, atomic absorption spectrometry; and NA, no analysis.

TABLE 11: SENSITIVITIES OF DIFFERENT METHODS FOR COAL ANALYSIS AS REPORTED BY DULKA AND RISBY [22]

	NAA[a] (g)	SSMS (ng)	CIMS[b] (g)	ICPAES ($\mu g/ml$)	NFAAS	XRFS (μg)	ASV
Ag	10^{-10}—10^{-9}	0.2		0.004	0.001 ng/ml	1.2	0.25 ppb
As	10^{-10}—10^{-9}	0.06				0.11	
B							
Ba	10^{-10}—10^{-9}	0.2		0.001	6×10^{-12}g	0.12	
Be		0.008		0.005	3×10^{-14}g		
Cd	10^{-9}—10^{-8}	0.3		0.002	0.03 ng/ml	0.40	0.005 ng/ml
Co	10^{-10}—10^{-9}	0.05	1×10^{-11}	0.003	2×10^{-12}g	0.05	
Cr	10^{-8}—10^{-7}	0.05	1×10^{-11}	0.001	1.2×10^{-12}	0.00006	
Cs	10^{-9}—10^{-8}	0.1				0.15	
Cu	10^{-10}—10^{-9}	0.08	1×10^{-11}	0.001	6×10^{-13}g	0.00002	0.005 ng/ml
Ga	10^{-10}—10^{-9}	0.09		0.014	1×10^{-12}g	0.01	0.4 ng/ml
Hg	10^{-10}— 10^{-9}	0.6		0.2	8×10^{-13}g	0.24	$4.0 \times 10^{-9}M$
La	10^{-11}—10^{-10}	0.1	5×10^{-11}	0.003	0.1 ng/ml	0.12	
Li		0.0006					
Mn	10^{-12}—10^{-11}	0.05	1×10^{-11}	0.0007	2×10^{-13}g	0.00015	
Ni	10^{-8}—10^{-7}		1×10^{-11}	0.006	4×10^{-13}g	0.06	0.1 g/ml
P						0.001	
Pb	10^{-7}—10^{-6}	0.3		0.008	0.002 ng/ml	0.0003	0.01 ng/ml
Rb						0.0075	
Sb	10^{-10}—10^{-11}						
Se							
Sn		0.3		0.3	2×10^{-12}g	3.9 ppm	2.0 ng/ml
U	10^{-10}—10^{-11}			0.08		0.00002	
V	10^{-11}—10^{-10}	0.04	1×10^{-11}	0.006	5×10^{-11}g		
Zn	10^{-8}—10^{-7}	0.1	1×10^{-11}	0.002	2×10^{-14}g	0.00004	0.04 ng/ml
Zr	10^{-8}—10^{-7}	0.1		0.005	5.0 $\mu g/nl$	0.00002	

[a] Sensitivity based on irradiation period of 0.5 T½ per 2 or 10 hr (whichever is less at a flux If 10^{13} neutrons $cm^{-2}S^{-1}$). Activity measured by Na/(Ti) gamma spectrometry.

[b] Chelation coupled with CIMS.

Table 11 shows sensitivities of different methods for coal analysis. It should be noted, however, that NAA and XRF can analyze samples, directly, whereas CIMS, ICPAES, NFAAS, and ASV, require the sample to be in solution, and SSMS requires the oxidation of the organic materials.

NAA: Neutron Activation Analysis
SSMS: Spark Source Mass Spectroscopy
CIMS: Chemical Ionization Mass Spectrometry
KPAES: Inductively Coupled Plasma Sources for Atomic Emission Spectrometry
NFAAS: Non-flame Atomic Absortpion Spectrometry
XRFS: X-ray Fluorescence Spectrometry
ASV: Stripping Voltometry

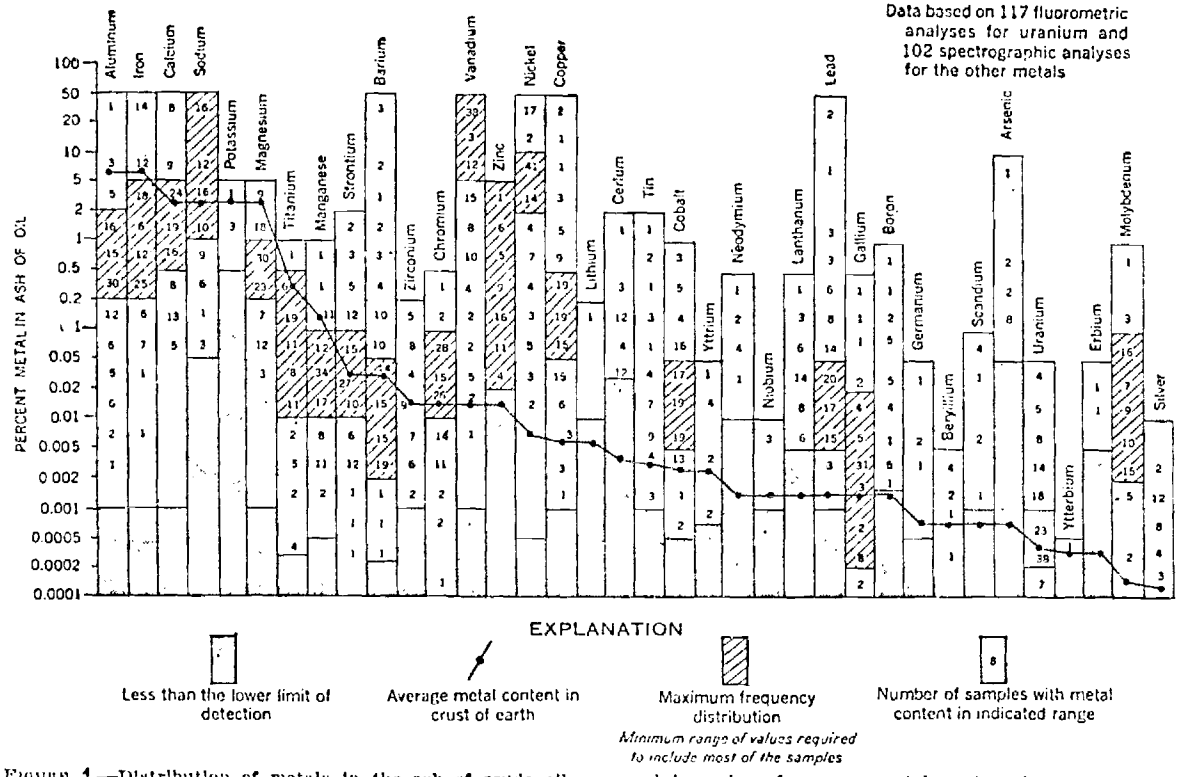


FIGURE 1.—Distribution of metals in the ash of crude oil arranged in order of average metal content in crust of earth, [4].

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Final Report

GEORGIA INSTITUTE OF TECHNOLOGY

CHARACTERIZATION OF NATURAL GAS, OIL AND COAL DEPOSITS WITH REGARD TO DISTRIBUTION DEPTH, AND TRACE ELEMENTS CONTENT

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CHARACTERIZATION OF NATURAL GAS, OIL AND COAL DEPOSITS WITH REGARD TO DISTRIBUTION DEPTH, AND TRACE ELEMENTS CONTENT

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ABSTRACT

Nearly all geologists and geochemists agree that natural gas and hydrocarbon fuels have been derived from organic matter. Increasingly, however, more and more geologists and geochemists are questioning the biological origin of hydrocarbon fuels. Evidence given in support of non-biological origin is as follows:

1. Methane rises from hydrothermal vents on the East Pacific Rise and from the Nyirogong lava lake in East Africa
2. When hot carbon comes in contact with H_2O at high pressure and low oxygen concentration, methane, CO and CO_2 are produced.
3. Gas trapped in diamond crystals found deep in the crust includes methane, CO, CO_2, ethane, propane and butane.
4. One geologist estimates that 100,000 tons of abiogenic methane is being released into the oceans every year.
5. Another group of geologists give an estimate of 1.4×10^{12} barrels of abiogenic oil being produced every million years for the past 700 million years.
6. The distribution of hydrocarbon fuels with regard to depth within the crust appears to correlate with coal being near the surface, oil in deeper wells and natural gas in deepest reservoirs.
7. The oldest oilfield is more than three times older than the oldest coal fields (1500 million to approximately 400 million years ago).
8. Some geologists correlate on a worldwide basis petroleum accumulations with regions that experienced diastrophism. This demonstrates a direct relationship between plate tectonics and petroleum accumulation.

Evidence given in support of a biological origin of hydrocarbons is as follows:

1. Nearly all accumulations of oil and coal are found in sedimentary rocks rich in carbon derived from the remains of living matter.
2. Petroleum contains "optically active" compounds, i.e., those which rotate a beam of light. Carbon compounds formed biologically are optically active whereas abiological compounds are not.
3. The presence of vanadyl and nickel porphyrins in certain oil is another strong point in favor of biological origin.

Giardini and Melton, two University of Georgia geologists, argue that all evidence in support of biological origin is inadequate and insist that the non-biological origin of oil is preferred.

In conclusion, it appears that neither proponents nor opponents of the biological origin of hydrocarbon fuel have adequate hard data to unequivocally establish beyond a shadow of a doubt a firm foundation for either case. The momentum, however, appears to be shifting toward more and more evidence for a non-biological origin.

With regard to radioisotope dating of coal, it appears that using uranium-thorium to lead decay is possible. One needs quantitative analysis of the relative amounts of U^{238}, U^{235}, thorium^{232}, Pb^{206}, Pb^{207} and Pb^{208} to determine the age of the coal.

I. INTRODUCTION

Nearly all geologists and geochemists agree that natural gas and hydrocarbon fuels have been derived from organic matter.[1] In the case of coal, some scientists of Argonne National Laboratory[2] claim to have discovered how nature made coal from lignin, the woody tissue in plant cell walls, and other organic matter such as lipids (fatty and waxlike substances from plants or algae). The general consensus regarding the biogenic origin of hydrocarbon fuels is not universally shared; however, some geologists and scientists, very few in number,[1,3,4,5,6] are beginning to question the biogenic origin. Porfir'ev published a paper in 1974 on the Inorganic Origin of Petroleum, in the Bulletin of the American Association of Petroleum Geologists. Gold[4] and Gold and Soter[5] have hypothesized that during the accretion of the earth material, 4.5 billion years ago, methane and other hydrocarbons were trapped and have been migrating from the depth to the surface ever since. Giardini and Melton[6,7,8] published several articles based on the analysis of gas trapped in diamond obtained from different geographical locations on the earth. They not only question the biogenic origin of hydrocarbon fuels, they argue for large accumulations of non-biogenic petroleum.

Interest in abiogenic methane has increased significantly after Welham and Craig[9] observed that methane was rising from hydrothermal vents on the East Pacific Rise. Also, Gerlack[10] observed that volcanic gases from Nyirogongo lava lake near Lake Kivu in east Africa was saturated with methane. Both sets of observations suggests that methane can be produced through magnetic processes. David Osborne[11] in an article in the Atlantic Monthly reports that Craig and colleagues have found methane streaming out of every ocean rift

and out of several underwater volcanoes. Craig estimates that a 100,000 tons of abiogenic methane is released into the oceans every year. The ratio of CO_2 to CH_4 streaming out of ocean rifts is about 100 to 1 according to Craig.

MacDonald[1] recently reviewed arguments for the biological origin of oil. He concluded that nearly all accumulations of oil are found in sedimentary rocks rich in carbon derived from remains of living matter. Also many oils contain "optically-active" compounds, i.e., those which rotate a beam of polarized light. Carbon compounds formed biologically are optically active whereas abiological compounds are not. The highest quantities of optically active compounds are found in the youngest oils and the least in the older oils. The presence of vanadyl and nickel porphyrins in certain oil is another strong point in favor of biological origin since porphyrins have been identified in pigments of both plants and animals. Finally, according to MacDonald,[1] the predominance in oils of compounds with an odd number of carbon atoms is strong evidence of biological origin because the biochemical synthesis favors such an arrangement.

On the other hand, Giardini and Melton[8] offer explanations that none of the arguments cited by MacDonald (and others) are valid "proof" of the biological origin of oils. For example, they state that the sedimentary rocks can easily contain traces of biologically recycled carbon compounds and that these rocks are permeable formations which act as migration channels for petroleum. Petroleum reservoirs are formed of sediments that have been deposited since the appearance of life on earth. Giardini and Melton assert that petroleum in general is composed predominantly of compounds which are not optically active. The presence of traces of optically active matter is not proof of a biological origin of petroleum.

With regard to the presence of nickel and vanadium porphyrins in petroleum, Giardini and Melton attribute this to the sedimentary environment which contained biological remnants; this should not be interpreted as proof of biological origin.

Other technical arguments with regard to the ratio of C^{12} to C^{13} are equally refuted by Giardini and Melton.

It appears that not enough data exist to totally refute the biogenic or abiogenic origins of hydrocarbon fuels. We know for a fact that in the case of methane some of it comes from non-biological origin. Does it all come from non-biological origins? We do not know. And what about oil and coal? Giardini and Melton found in diamond hydrocarbon chains up to C_4H_{10} which are attributed to a non-biological origin. This fact points to the possibility that petroleum also could come from polymerization of smaller chains of hydrocarbon. Again, we do not know how much if any oil comes from non-biological origins but the possibility exists. With regard to coal the picture is murkier. We have not been able to uncover any relationship between coal and oil or coal and gas. Two facts however point to the possiblity that even coal could have a non-biological origin:

1. As a function of depth, it appears that coal is on top, petroleum is in the middle and natural gas is at the bottom.
2. The distinction between some thick oils and asphalt decreases as the volatiles in oil escape. There might be a similar relationship between asphalt and coal.

Now, if polymerization played a part in the creation of oil from natural gas then it is reasonable to speculate that where geologic formations allow, in so far as permeability, temperature, pressure and local physical and chemical conditions, the volatile components of the petroleum to escape, the resulting

residuals would be tending toward the thicker oils, asphalt, coal, and maybe even graphite. The fact that coal beds tend to be closest to the surface where it is relatively easier for volatiles to escape is one reason why the possibility for a connection between methane and coal through polymerization and other chemical reactions cannot be excluded.

The general acceptance of a biological origin, which has been firmly entrenched for a long time, is slowly giving in to more scrutiny and increasingly we see more and more people question the biological origin.

With regard to where or how hydrocarbons came into being, the opinions differ widely. For example, T. Gold [11] believes that all of it is premordial in origin, trapped within the earth from the beginning of time and is being released from the depth to the surface ever since. Mr. Gold further believes that natural gas is the result of heavier oils breaking up under the effects of high temperature into simpler structures principally methane and residuals like coal or pure carbon. This hypothesis is opposite of that which puts methane as the building block and the polymerization and other chemical reactions produces both oil and coal.

A.A. Scarborough[12] has published his work on the origin of the solar system and has hypothesized that hydrocarbon fuels are being made <u>continuously</u> by a nuclear furnace in the core of the earth. Mr. Scarborough does not offer any terrestrial evidence supporting his hypothesis.

MacDonald alluded to the fact that natural gas can be produced by magmatic processes and gave evidence that when hot carbon comes in contact with H_2O under high pressure, methane, CO and CO_2 are produced. By analogy, when hot steam is brought into contact with graphite or coal, in the absence of oxygen, methane and oil are produced. This is called "synfuel."

Giardini and Melton[8] proposed a model in which continuous outgassing of H_2, CO, CO_2, alcohol, and low order hydrocarbons, up to butane are entrained over appropriate catalysts to form a variety of hydrocarbons. The flow channels for these products from the mantle to crustal traps follow faults traceable to lithosphere fracture. Petroleum bearing regions are found in association with land masses that experienced rifting, orogeny by subduction or collision. Adjacent regions for sediment generation and accumulation are produced by the resulting differential elevation of surface. Tectonically active regions undergo diastrophism, which produces reservoir structures in the sediments. Tectonically produced faults and fissures tend to generate deep seated fractures that penetrate the lithosphere and enable flow of the mantle fluids to the sedimentary reservoirs.

Giardini and Melton[8] estimate that the upper limit for petroleum production per million years for the past 700 million years is 2.1×10^{11} tons or 1.4×10^{12} barrels/million years. Of this amount only 0.2% is retained in reservoirs.

Another fundamental question with regard to migration of carbon from the mantle to the surface is whether or not elemental carbon exists in the magma. We know that diamond exists in diamond mines, therefore elemental carbon must also exist. Under elevated temperatures and high pressure, carbon can strip the hydrogen from water molecules to make natural gas. Under this scenario one is able to explain better the fact that natural gas fields tend to be deeper than those of oil and coal.

In summary, our survey of the literature shows that increasingly more and more geologists and geochemists are questioning the biological origin of hydrocarbon fuels. The non-biological origin is also being increasingly promoted to explain natural phenomena which could not be explained otherwise.

In this report, the characterization of natural gas and oil wells and coal beds is reviewed with emphasis on Pennsylvania's coal, petroleum, and natural gas. We also review possible methods for radiometric dating of coal and petroleum.

II. NATURAL GAS AND OIL WELLS AND COAL BEDS CHARACTERIZATION

Coal, petroleum, and natural gas are widely distributed on the face of the earth. Because of the economic importance of these fuels, there is a vast amount of detailed information about their occurrences available in the open literature. Additionally, a great deal of proprietary information is held by companies involved in exploration for and extraction of the fuels, and many foreign governments have data about their fuel deposits that is not freely available.

Because of the great interest in the world's fuel resources, there are many articles and books that provide summaries of the available information. For example, the Encyclopaedia Brittanica (15th Edition, 1983) has authoritative articles entitled "Coals" and "Petroleum," which provide excellent, brief introductions to the character of these materials and their occurrences in the earth's crust. Examples of recent books that provide more thorough summaries of the character and distribution of fuels in the earth are those by Ward[13] and Tiratsoo[14]. Both coal and petroleum fields usually have natural gas associated with them, but there are many other occurrences of natural gas. MacDonald[1] has written a thorough review of the origins of natural gas.

Because of the vast amount of information available about the occurrence of fuels in the earth's crust, it is obviously not possible for this report to be complete as a compilation of such data. Nor would it be appropriate for the authors to attempt a broad summary of the available information, for there are

already available summaries of this sort written by experts who have devoted their careers to evaluation of fuel resources. The sponsor of the research that this report represents is interested in the possibility that some of the fuels within the earth may not be of biological origin. For this reason, the focus of this report will be on certain aspects of the occurrence of natural fuels that relate particularly to the possibility of non-biological origin of fuels.

We will look at the geographical distribution of the fuels at several different levels, beginning with a brief summary of the worldwide patterns of their occurrences, which should convey several important ideas:

- Fuels in the earth's crust are very broadly distributed in the continental portions of the earth's crust (including the submerged continental margins) but coal and petroleum have not been found in the oceanic crust.
- Although broadly distributed in the continental crust, the fuels are distributed in ways that are far from uniform.
- Although some regions have both coal and petroleum, these two kinds of fuels are not generally associated with one another.

Along with the summary of the worldwide distribution of fuels, it is quite important to consider the geological aspects of the occurrence of the fuels. It is, of course, the geological associations of these fuels with particular kinds of rocks, formed within restricted ranges of time, that appear to govern the geographical distribution of the fuels. Important generalizations are:

- Fuels have been found almost exclusively in association with sedimentary rocks.

- Coal has not been found in rocks older than 400 million years and oil has not been found in rocks older than 1500 million years. Most major occurrences of these fuels are in rocks formed within the last 350 million years of earth history.

We will also give a brief summary of the geographical distribution of the fuels in the 48 conterminous states of the U.S., since the geography of these states is likely to be much more familiar to those who will read the report than is world geography. But in this case, as for the world as a whole, the information is far too vast for a detailed accounting. Consequently, we will focus on one state, Pennsylvania, which has major occurrences of coal, petroleum, and natural gas.

II.1 Worldwide Distribution of Coal, Oil, and Natural Gas: A Summary

Coal, petroleum and natural gas are very broadly distributed in the continental part of the earth's crust, which includes the continents, the submerged continental margins (continental shelves), and all of the world's large islands except Iceland and Hawaii. These two islands are part of the earth's oceanic crust, which comprises all of the deep ocean floor as well as most of the small oceanic islands.

Although oceanic crust underlies more than half of the earth's surface, it is not known to contain any coal deposits nor any economically useful accumulations of petroleum. However, the high pressure and low temperature of deep ocean water permit methane hydrates to be stable in deep ocean sediments, and there is growing evidence that large quantities of methane may be present in such sediments [MacDonald[(1)]]. Methane is also known to be present in volcanic gases and hot waters associated with the volcanic activity that is continually producing new oceanic crust. The concentrations of methane associated with volcanic activity are low and do not appear to be of any economic importance, however.

Our knowledge of the character of the oceanic crust has vastly increased in the past four decades because of intense study of the sea floor by remote sensing methods, because of direct sampling of the sea floor by shallow coring and dredging and later by deep-sea drilling, and because of detailed geological studies of islands where oceanic crust reaches above sea level. Nevertheless, we have far less information about the oceanic crust than about the continental crust. For this reason, and because coal and petroleum appear to be limited in their occurrences to the continental crust, the remainder of this summary deals with the distribution of fuels in the continental crust.

II.1.1 World Coal Resources

Coal occurs in all of the continents (even in Antartica, although it is not produced there) and in many of the world's large islands [Ward[13]]. It is not uniformly distributed, however, but is concentrated in certain sedimentary basins whose areal extent is a small fraction of the total land area of the earth. Most of the world's coal is in three large countries, the USSR, the USA, and China. Africa and South America have much less coal than do the northern continents.

The world's coal resources have been estimated to be greater than 10 trillion tons, of which about 1 trillion tons are recoverable under present conditions [Ward[13]]. For comparison, the total production of coal in 1981 was about 4 billion tons, so recoverable reserves are several hundred times greater than current annual production. The USA has long been the world leader in coal production. It produced more than 700 million tons of coal in 1981, but the USSR and China were not far behind. In terms of proved reserves, coal is much more abundant than petroleum, and even though past estimates of the world's total petroleum resources have been notoriously inaccurate, there is little reason to doubt that coal is an order of magnitude more abundant than petroleum in the earth's crust.

II.1.2 Worldwide Petroleum Resources

Petroleum is more broadly distributed than is coal in the earth's continental crust. The broad distribution is evident by examination of a table showing world oil production by country in 1982 [Tiratsoo[14] Table 1/6 in which all of the larger countries of each continent except Africa (and, of course, Antartica) are listed as significant oil producers. Although petroleum is broadly distributed, it is by no means uniformly distributed. About half of the world's proved recoverable oil reserves are in the Persian Gulf area within a region roughly a million square kilometers in area, about 0.2 percent of the earth's entire surface area [Tiratsoo[14], Table A/9 and figure 4/1].

As is coal, petroleum is found in sedimentary basins, rather than in portions of the earth's crust where uplift and erosion have exposed large areas of plutonic igneous and metamorphic rocks. Tiratsoo[14] [Table 1/19] has listed 580 known sedimentary basins, of which 364 have no production of petroleum. Neither coal nor petroleum is ubiquitous in sedimentary basins, and, although some basins have both coal and petroleum, many basins have one but not the other. For example, coal is insignificant in the Persian Gulf area where petroleum is so abundant, while South Africa has major coal resources and no petroleum.

The proved recoverable oil reserves of the world total about 700 billion barrels. The U.S. Geological Survey has recently begun an effort to estimate the undiscovered recoverable resources of petroleum in every sedimentary basin of the world that is considered to have petroleum potential [Masters[15]]. There are necessarily wide ranges in estimates of this sort, but the most liberal estimates (assigned a five percent probability by the U.S. Geological Survey) provide a total for such undiscovered petroleum that is similar to the total of proved reserves, more than 500 billion barrels but less than one

trillion barrels. These estimates do not include the massive amounts of heavy hydrocarbons that occur as (currently) unproducible heavy oils or tar sands. More than one trillion barrels of such heavy hydrocarbons occur in Venezuela alone. The Athabaska tar sands of western Canada contain hydrocarbons in an amount comparable to the world's proved reserves of recoverable petroleum, about 700 billion barrels.

The United States was the world leader in petroleum production until about 1970 when its production was surpassed by that in the Middle East. Subsequently the Soviet Union has become the world leader in petroleum production. Unlike the Middle East and the Soviet Union, where proved reserves are far greater than total production to date, the United States has much less petroleum remaining in proved reserves than the total of its production during the past. Although in total (production plus proved reserves) the U.S. has had more petroleum than Mexico, Mexico now has greater reserves than the U.S. and follows the Middle East and the USSR in terms of proved recoverable reserves.

II.1.3 The Worldwide Distribution of Natural Gas

As noted earlier, natural gas normally occurs in association with accumulations of petroleum and in coal beds. Of these two kinds of occurrence, the gas associated with petroleum has been by far the most important economically; about 30 percent of the commercially useful natural gas in the world occurs in association with oil [MacDonald[1]]. The methane associated with coal beds has been primarily an unwanted byproduct of coal mining, but serious efforts are underway to utilize coalbed methane resources in the U.S., particularly in certain cases where the methane is abundant but the coal cannot be produced economically [Rightmire[16] and others]. The geographical distribution of these kinds of natural gas resources is of course the same as that of the petroleum and coal with which the gas is associated, which has

already been described. In addition, there are many occurrences of natural gas that is not associated either with petroleum or coal, and these occurrences are quantitatively the most important.

The largest gasfields of the world are in the West Siberian Basin of the USSR, where identified recoverable gas reserves are about 700 trillion cubic feet [Tiratsoo[14]]. A similar quantity of natural gas remains undiscovered in this basin, according to Clarke[17] and others. Thus, this basin holds a substantial fraction of the world's total recoverable resources of natural gas, which have been estimated by MacDonald[18] to be about 10 quadrillion cubic feet. The Middle East also has a substantial fraction of the world's gas resources.

Hunt[19] has estimated that the amount of gas dispersed in sedimentary rocks is 10 to 200 times that which occurs in economically useful accumulations, and MacDonald[18] has suggested that the amount of methane stored in methane hydrates may be more than one thousand times greater than the world's reserves of recoverable natural gas. It should be noted that even greater quantities of solid organic material occur dispersed in the world's sedimentary rocks. This material is neither coal nor petroleum nor natural gas, but it is the predominant form of reduced carbon in the crust of the earth. The amount of carbon dispersed in sedimentary rocks is estimated to be of the order of 10^{16} tons, roughly a thousand times more than that present in economically useful concentrations as coal, petroleum, or natural gas.

II.1.4 Age and Character of the Rocks Associated with Natural Fuels

Virtually all of the economically useful accumulations of natural fuels that have been found in the earth are in sedimentary basins, and so the association of fuels with sedimentary rocks is a very strong one. The fuels do sometimes occur within or in contact with igneous rocks, but in nearly all such

cases the igneous rocks have been intruded into or have been extruded over pre-existing sedimentary rocks; such cases do not affect the generality of the association of fuels with sedimentary rocks.

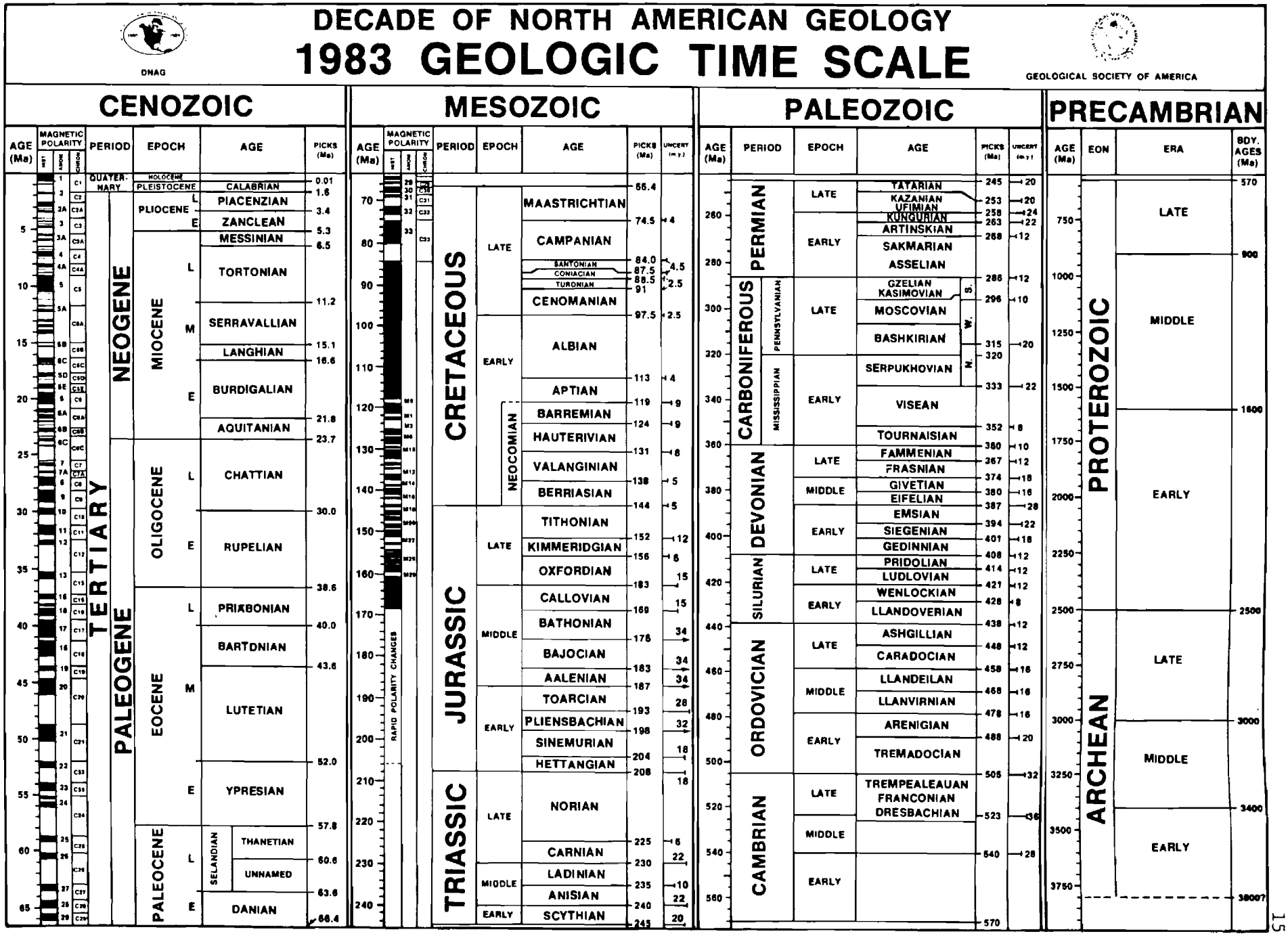
Coal is found only in sequences of sedimentary rock (including metamorphic rocks that have been formed by metamorphism of sedimentary rocks) and is considered by geologists to be itself a sedimentary rock. The geological evidence for this genetic classification of the material is not simply the universal association of coal with sedimentary rocks, but rather the evidence derives from the structural and stratigraphic relationships between the coal and the sedimentary material that surrounds the coal, and from the petrographic characteristics of the coal itself. Some of the more important aspects of this evidence are as follows:

- "Hardly any coal seam consists of pure coal substance; nearly everywhere the coal is interlayered with stratified impurities (usually shale)." [van Krevelen[20]] The character of these non-coal 'bands' or 'partings' and their stratigraphic relationship to the coal are strong evidence for the sedimentary origin of coal [Ward[13]].
- On a larger scale, the commonly observed splitting and coalescence of coal seams and the discontinuous nature of many coal seams are features consistent with their origin in a complex sedimentary environment (for example, a major river delta) where there were continual changes in the local environment as a consequence of changes in positions of river channels and shorelines.
- Unlike volcanic rocks formed from extruded lava, which are often associated with dikes or plugs that clearly cut across the structure of the rocks through which the molten magma moved, coal is not observed to be associated with cross-cutting bodies of similar composition. (On

the other hand, asphalt commonly occurs in veins that cut across pre-existing rocks [Hunt[21] and others], evidence that it has moved as a liquid). In cases where magma has intruded across and into coal seams, the coal has been quite distinctly altered by loss of volatile constituents [Ward[13]], which suggests that the coal had never been exposed to high temperatures except where it is in proximity to the igneous rock.

- The fine structure of coal shows it to have a texture that is consistent with a sedimentary origin. The texture is quite different from the texture of rocks that have demonstrably formed by solidification of a liquid. One of the most important observations of coal petrography is the common occurrence of the well-preserved structures of plant cells, spores, and algae. Unlike macroscopic plant fossils, which are generally more abundant in shaly partings than in the coal itself, the microscopic plant remains are part of the coal macerals--the essential substances of the coal itself [van Krevelen[20]].

The occurrence of coal is notably restricted in time, that is, in respect to the ages of the rock sequences that contain coal. (Table 1 is a recent version of the geological time scale, reproduced here to show the relation of the various geological time periods to one another and the approximate absolute time interval with which each is associated.) The oldest coal-bearing strata were deposited in the Devonian Period, not more than about 400 million years ago. (A carbonaceous material called shungite occurs in older metasedimentary rocks in Fennoscandia, but this material is thought to have been asphalt originally rather than coal.) Nearly all coal is found in rocks formed during or after the Carboniferous Period, which began about 350 million years ago.


DECADE OF NORTH AMERICAN GEOLOGY
1983 GEOLOGIC TIME SCALE
DNAG
GEOLOGICAL SOCIETY OF AMERICA
CENOZOIC
MESOZOIC
PALEOZOIC
PRECAMBRIAN
AGE (Ma)
MAGNETIC POLARITY
PERIOD
EPOCH
AGE
PICKS (Ma)
UNCERT (m.y.)
EON
ERA
BDY. AGES (Ma)
QUATERNARY
TERTIARY
NEOGENE
PALEOGENE
HOLOCENE
PLEISTOCENE
PLIOCENE
MIOCENE
OLIGOCENE
EOCENE
PALEOCENE
CALABRIAN
PIACENZIAN
ZANCLEAN
MESSINIAN
TORTONIAN
SERRAVALLIAN
LANGHIAN
BURDIGALIAN
AQUITANIAN
CHATTIAN
RUPELIAN
PRIABONIAN
BARTONIAN
LUTETIAN
YPRESIAN
SELANDIAN
THANETIAN
UNNAMED
DANIAN
CRETACEOUS
JURASSIC
TRIASSIC
LATE
EARLY
NEOCOMIAN
MIDDLE
MAASTRICHTIAN
CAMPANIAN
SANTONIAN
CONIACIAN
TURONIAN
CENOMANIAN
ALBIAN
APTIAN
BARREMIAN
HAUTERIVIAN
VALANGINIAN
BERRIASIAN
TITHONIAN
KIMMERIDGIAN
OXFORDIAN
CALLOVIAN
BATHONIAN
BAJOCIAN
AALENIAN
TOARCIAN
PLIENSBACHIAN
SINEMURIAN
HETTANGIAN
NORIAN
CARNIAN
LADINIAN
ANISIAN
SCYTHIAN
RAPID POLARITY CHANGES
PERMIAN
CARBONIFEROUS
DEVONIAN
SILURIAN
ORDOVICIAN
CAMBRIAN
PENNSYLVANIAN
MISSISSIPPIAN
TATARIAN
KAZANIAN
UFIMIAN
KUNGURIAN
ARTINSKIAN
SAKMARIAN
ASSELIAN
GZELIAN
KASIMOVIAN
MOSCOVIAN
BASHKIRIAN
SERPUKHOVIAN
VISEAN
TOURNAISIAN
FAMMENIAN
FRASNIAN
GIVETIAN
EIFELIAN
EMSIAN
SIEGENIAN
GEDINNIAN
PRIDOLIAN
LUDLOVIAN
WENLOCKIAN
LLANDOVERIAN
ASHGILLIAN
CARADOCIAN
LLANDEILAN
LLANVIRNIAN
ARENIGIAN
TREMADOCIAN
TREMPEALEAUAN
FRANCONIAN
DRESBACHIAN
PROTEROZOIC
ARCHEAN
LATE
MIDDLE
EARLY

The absence of coal in rocks older than 400 million years has been interpreted as a consequence of the virtual absence of land plants on earth prior to that time. Coal is not evenly distributed in rock younger than 350 million years; rather it is much more abundant in rocks of late Paleozoic age (roughly from 250 to 350 million years old) and in rocks of late Cretaceous and Tertiary age (less than 100 million years old) than it is in rocks formed in the period between these age groups.

Petroleum and natural gas are fluids that migrate through permeable rocks, and the evidence that these materials may have originated from organic sedimentary material is quite different in character from the evidence that coal is a sedimentary rock. Since the fluid fuels have generally moved through permeable rock until trapped by some sort of relatively impermeable barrier, the structure and texture of the rock that contains the fuels--the reservoir rock--are usually unrelated to the origin of the fuels. For example, natural gas has been produced from volcanic rocks (vesicular basalts) of the Columbia Plateau in Washington; the gas presumably originated in coal-bearing sediments below the basalt [Swain(22)].

Traditional geological methods cannot pinpoint the origin of the fluid fuels. The belief held by most geologists that petroleum and most natural gas deposits originate from organic material in sedimentary source rocks is based on a complex set of data that includes a great deal of chemical and isotopic information as well as a vast amount of information from geological and engineering studies in the oilfields. The fact that these fuels have been found in significant quantity only in sedimentary basins is an important part of the case for their sedimentary origin but is by no means the whole story. One might question this part of the evidence on the ground that virtually no exploration for petroleum has occurred outside of the world's sedimentary

basins, but it should be noted that discovery of many oilfields, particularly in the early days of the petroleum industry, was aided by the presence of natural seeps. Such occurrences have not been noted outside of the sedimentary basins.

Petroleum and natural gas are often found in rocks older than the oldest coal-bearing rocks, and in a few cases petroleum-bearing rocks are of Precambrian age, more than 600 million years old. The world's oldest oil may be that found in Australian rocks about 1500 million years old [Cook[23] and others]. Significant accumulations of gas and petroleum have been found in Precambrian rocks in Eastern Siberia. Of course, the age of a reservoir rock is not the same as the age of the petroleum or gas that it contains. But since these fluids generally move upward through the earth's crust, and since in sedimentary basins older rocks are normally below younger rocks, there is reason to believe that the source of an accumulation of petroleum or natural gas is generally as old as or older than the reservoir rock. Natural gas is rather commonly found and petroleum is sometimes found in rocks of early Paleozoic age, but the fuels are more abundant in younger rocks. Rocks of Mesozoic age are particularly important as producers of petroleum (in contrast to their relatively small importance for coal).

In summary, the portions of the earth's crust that are known to contain coal and petroleum are restricted in geographical distribution and in the character and age of the rocks in which the fuels occur. Our known coal and petroleum resources occur only in sedimentary basins, coal in rocks not more than 400 million years old and petroleum in rocks usually less than 400 million years old but sometimes in older rocks (as much as 1500 million years old). These fuels are unknown in portions of the continental crust comprising plutonic rocks or very old sedimentary rocks, as well as in the entire oceanic

crust. Natural gas may be somewhat more broadly distributed, particularly as methane hydrates in oceanic sediments, but the gas known to be recoverable by present technology is restricted in its distribution in the same way as petroleum.

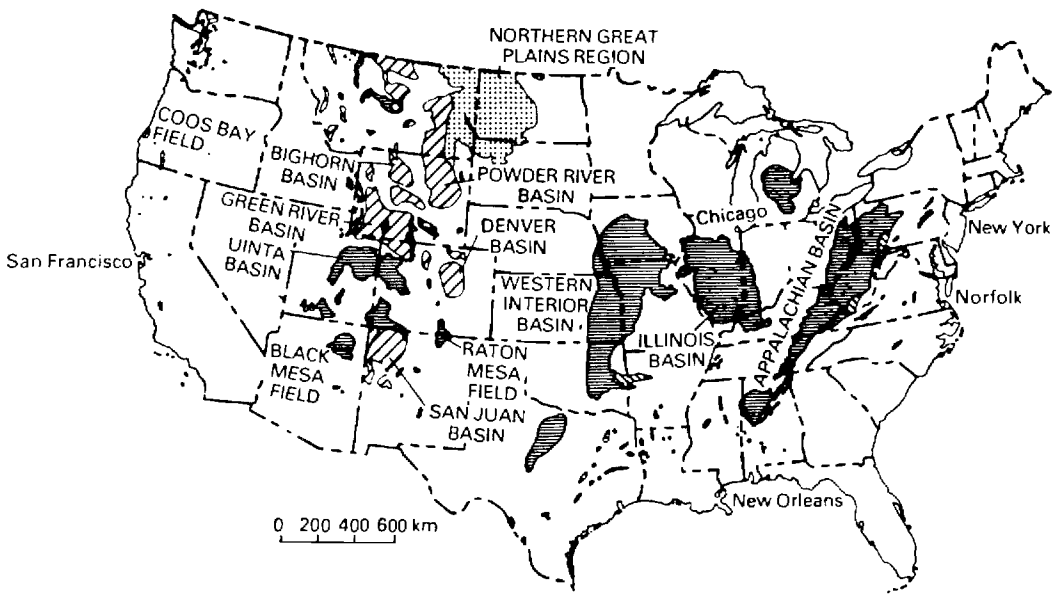
II.2 Coal, Petroleum, and Natural Gas in the United States: A Brief Summary

II.2.1 Coal

Ward[13] has given a brief summary of the geographical and geological distribution of coal in the United States and has cited examples of recent literature that give detailed information on specific areas. A map by Averitt[24] showing the distribution of coalfields in the conterminous United States is reproduced here as Figure 1. Coal-bearing strata occur in 37 states and underlie about 13 percent of the land area of the U.S. The major coalfields are in the Appalachian Mountain region, the Rocky Mountain region, and a few basins in the continental interior. Although there are numerous exceptions, there is a general decrease in rank of coal going from east to west in the United States. Also, the coals of the eastern U.S. are mostly in strata of Pennsylvanian age, whereas those of the western states are mostly in younger (Cretaceous and Tertiary) strata.

Anthracite occurs in the Appalachian fold belt where strong tectonic activity subjected the coal to high temperature as a consequence of deformation and deep burial. The major anthracite fields are in eastern Pennsylvania and in the Narragansett Basin of Rhode Island and Massachusetts. Great quantities of bituminous coal occur in the Appalachian Plateau region and in the Illinois Basin. Higher rank (low-volatile) bituminous coal is found in the eastern part of the Appalachian Plateau and in some adjoining parts of the Appalachian Ridge and Valley province where moderate tectonic activity caused the coal to be affected by somewhat elevated temperatures. High-volatile bituminous coal

FIGURE 1



Distribution of coalfields in the conterminous United States ■ Anthracite and semi-anthracite; ▨ low volatile bituminous coal; ▬ medium and high volatile bituminous coal; ▨ sub-bituminous coal; ▨ lignite (Averitt 1975).

predominates in the western part of the Appalachian Basin and in the Illinois Basin. Although the abundant coals of the eastern U.S. are of late Palezoic (mostly Pennsylvanian) age, there are some younger coals in this part of the country. Low-rank coal occurs in rocks of early Mesozoic age in small sedimentary basins within the Appalachian Piedmont region, and lignite is widespread in Tertiary sedimentary rocks of the Gulf Coastal Plain.

Coals of the western U.S. and Alaska are generally of lower rank than the Appalachian deposits. The most extensive coals of the western U.S. are in beds of late Cretaceous age in several large basins and numerous small basins in the Rocky Mountain region. These are mostly of high-volatile bituminous and sub-bituminous rank. In some of these basins, coal seams are present in beds of Tertiary age overlying the Cretaceous deposits; coal and lignite of Tertiary age also occur in other basins in the western U.S. The most important area of Tertiary coals is the western Washington coal region, the only major area of coal occurrence in the far-western states.

None of the major coal deposits of the eastern U.S. are deeply buried. The bituminous coals of the Appalachian Basin and the Illinois Basin are distributed throughout the uppermost sedimentary rocks of these basins, extending downward only a few thousand feet. Except at the southern end of the Appalachians in Alabama, where coal-bearing strata may be deeply buried under thick sediments of the Gulf Coastal Plain, and in the anthracite-bearing Appalachian fold belt, where strong tectonic deformation has caused portions of the coal beds to be deeply down-folded, the deepest Appalachian coal beds are only about 2300 feet below the surface. In the Illinois Basin, all the coal seams are within 3000 feet of the surface and the major coals are within 1500 feet of the surface [Archer[25] and Kerr].

The tectonic character of the Rocky Mountain region has led to thick accumulations of sediments in the intermontane basins. Consequently, even though the coal-bearing strata of this region are younger than those in the Appalachians, the coal in some of the Rocky Mountain basins extends to much greater depths than does the coal in the main part of the Appalachian Basin. Overburden as thick as 10,000 feet occurs over coal in parts of the Piceance Basin of Colorado [Choate[26] and others]. Such deeply buried coal beds may become quite important for the methane they contain, even though they are too deeply buried for coal mining to be practical [Rightmire[16] and others].

II.2.2 Petroleum

As in the world as a whole, petroleum in the United States is more broadly distributed than is coal. Petroleum accumulations are found in most of the coal-bearing basins, but the greatest oilfields are not associated with coal. The major oilfields of the U.S. are not in the basins where coal is important. Ten of the twelve largest oilfields of the U.S. are in Texas and California where coal is not significant [Tiratsoo[14], Tables 7/8 and 7/18]. The other two (of the top twelve) are the great Prudhoe Bay field in Alaska and one in southern Oklahoma; neither of these is in a coal-bearing area. The Louisiana Gulf Coast is another major region of oil production that is not associated with coal.

Major petroleum accumulations are generally at greater depths than the major coal deposits of the U.S., although some of the earliest-discovered oilfields extend quite close to the surface. According to Tiratsoo[14] most oils and gas accumulations are at depths of 2000 to 10,000 feet, but sustained production has been established to depths as great as five miles. The ages of the rocks containing petroleum also vary more broadly than those of coal-bearing rocks. Particularly in the Appalachian region and the

midcontinent, petroleum often occurs in reservoir rocks that are older than the oldest coal-bearing strata. Petroleum reservoirs of Devonian and Silurian age are common in the Appalachian region, and even older (Ordovician) strata are important reservoirs in the midcontinent. In sharp contrast are major oilfields in California in thick, very young (Pilocene) sequences of sediments formed by rapid sedimentation in a tectonically very active region.

II.2.3 Natural Gas

Natural gas is always present in association with coal and petroleum, except where they are so close to the earth's surface that the gas has been able to escape. Hence, the foregoing summaries of the distribution of coal and petroleum in the United States are also pertinent to the distribution of natural gas. But natural gas has many occurrences where it is not associated with coal or petroleum.

As was noted above the natural gas has been obtained from volcanic rocks in Washington State, but the normal occurrence of natural gas that is not associated with oil or coal is in the sedimentary basins. It often occurs as a gas phase within permeable sedimentary rocks that are capped by impermeable rocks that prevent the gas from escaping. Such gas reservoirs are structurally like petroleum reservoirs. There is a variety of reasons why such reservoirs may often contain gas but no oil, but the factor most universally recognized as important is the effect of depth and the geothermal gradient (that is, the increase of temperature with increasing depth in the earth). Natural gas is commonly found at greater depth than is oil within a given petroliferous region, presumably because gas is stable at temperatures that are (or were) too high for petroleum to exist. The common occurrence of gas at greater depth than petroleum is not to be confused with the vertical relationship of oil and free (that is, undissolved) gas in any particular petroleum pool where both

occur; in such cases the free gas is always above the oil because the oil is more dense. The same reasoning is also applicable to gas pools in rocks that now are fairly close to the surface but were once deeply buried, as in parts of the Appalachian Mountains where erosion has removed a great deal of the original sedimentary cover.

The accumulation of sediments is not the only way in which rocks become deeply buried. Important occurrences of natural gas occur in rocks that have been buried by the action of great thrust faults where thick sheets of rock have been pushed laterally over sedimentary layers that were originally near the surface. Both petroleum and gas occur in the Western "overthrust belt," including an interesting recent discovery of a major gas pool below crystalline Precambrian rocks that have been thrust over younger sedimentary rocks. There is considerable interest in the possibility that similar occurrences might be present in the "eastern overthrust belt," which includes at least a part of the Appalachian Piedmont region, once thought to be outside the realm of exploration for oil and gas.

In addition to the natural gas that is present in reservoirs from which it is recoverable by present technology, the United States may have vast quantities of natural gas in other forms. These include methane hydrates in deep waters offshore and perhaps in the Alaskan tundra, gas dissolved in formation water under high pressure deep underground, and possibly significant amounts of gas from deep within the earth, which might have accumulated in regions that have not been explored for fuels.

II.3 Coal, Petroleum, and Natural Gas in Pennsylvania

Pennsylvania has been a world leader in coal production for well over a century and has been a significant producer of oil and natural gas since the world's first modern oil well was drilled there in 1859. In a large area of

western Pennsylvania, there are important accumulations of all three fuels, but the vertical distributions of each of the three fuels differs from that of the others. In the state as a whole, there are also important differences in the area distributions of the fuels.

As noted in the preface, there is a vast amount of information on the worldwide distribution of natural fuels, and so this report will use information about the distribution of fuels in Pennsylvania as a convenient example of the complexity of the geographical and geological distibution of the materials. Even for this one state, the amount of information available is far too great for a report of practical size to be complete. For example, there are more than 25,000 wells in the giant Bradford oil field (which extends from Pennsylvania into New York State) alone [Tiratsoo[14]]. So this part of the report, on fuel occurrences in Pennsylvania, is also necessarily a summary.

II.3.1 Coal

Coal is broadly distributed in Pennsylvania, from anthracite fields in the eastern part of the state to the bituminous fields that occupy most of the Appalachian Plateau in the western part of the state (Keystone Coal Industry Manual, 1974, Figure 1). In comparison to the main bituminous field, the anthracite fields are small and discontinuous, a consequence of the effect of severe folding of the sedimentary strata in the eastern part of the state (at the close of the Paleozoic Era) and subsequent erosion of much of the original rock. There are scattered coal fields in the central part of the state, where the strata are more gently folded than those further east. In the western third of the state--the Appalachian Plateau province--the coal-bearing strata were beyond the direct influence of the tectonic stresses that folded the rocks further to the east, so the sedimentary strata are little changed in orientation from the nearly horizontal attitude in which they were deposited.

But this area, the main bituminous coal field, is not structureless; there are gentle troughs and swells and the entire region forms a structural basin that deepens southwestward. The deepest part of this "spoon-shaped" basin, which extends across western West Virginia and eastern Ohio, is in the southwestern corner of Pennsylvania and the adjoining portion of West Virginia. The deepest coal seams there are about 2300 feet below the surface. These coal seams, the lowermost ones in the stratigraphic sequence, are found at generally shallower depths as one moves northward across the western part of the state until, in the counties that border on New York State, there are only scattered occurrences of coal, close to the surface.

In the major bituminous fields there are dozens of individual coal seams, variable in thickness but typically reaching maximum thicknesses of three to six feet. These seams are distributed within a sequence of sedimentary rock that is more than 2000 feet thick in the southwestern corner of the state. The Keystone Coal Industry Manual (1981) shows 39 coal seams in the main bituminous field, distributed within a sequence of rocks whose cumulative average thickness is 2400 feet. Such a listing of coal seams is a generalization that focuses on the major seams that can be identified by correlation over broad areas; it does not include many minor occurrences of coal, not does it indicate the complexity that is characteristic of coal distribution--the tendency of coal beds to be discontinuous or at least to be quite variable in thickness, and the common splitting and coalescence of coal seams. For example, the oldest coal-bearing series of strata in Pennsylvania, the Pottsville Group, has ". . . a sporadic occurrence of coals with highly variable thicknesses and limited lateral extents. The main coals of this group are, in ascending order: the Sharon, Quakertown, and Lower and Upper Mercer" [Adams[27] and others]. Only the four main coals of the Pottsville Group are shown in the Keystone compilation.

The rank of coal varies systematically from anthracite in eastern Pennsylvania to high-volatile bituminous coal in the western part of the state. There is also some variability in rank to be expected with depth in the westernmost part of the state where there has been little tectonic disturbance. But the east-to-west variability in rank is much greater than any vertical variability, a consequence of the history of tectonic deformation and erosion that has brought once deeply buried coals to the surface in eastern and central Pennsylvania.

Most of the coals in Pennsylvania are in strata that were deposited during the Pennsylvanian Period. In the southwestern corner of the state, however, coal occurs in the Dunkard Group, which is at least partly of Permian age. The sedimentary rocks that contain the coals include both marine and nonmarine strata. These sandstones, shales, and limestones record a complex history of sedimentation that includes alternating periods of marine transgression and of fluvial delta growth seaward as clastic sediments were carried westward from the early Appalachian Mountains.

II.3.2 Oil

Oilfields are spread throughout the western portion of the main bituminous coal field in Pennsylvania, but there are only scattered occurrences of oil in the eastern portion of this large coal field. Except in the extreme southwestern corner of the state, where oil occurs in sandstones of the Pennsylvanian Conemaugh Group, wherever oil and coal occur in the same area of the state, the oil is in strata that are older, and thus below, the coal-bearing strata [Ver Wiebe[29]]. The oilfields are not limited to the coal-bearing part of the basin; they extend northward beyond the coal fields into southwestern New York State. The giant Bradford oilfield is in this area north of the coal fields, where the rocks now exposed at the surface are older than the coal-bearing rocks.

The oilfields of Pennsylvania are generally associated with swells--very gently folded anticlinal structures--in the Appalachian Plateau region, where oil is trapped in permeable sandstones beneath impermeable formations. However there are many cases where oil has been found in isolated sand bodies surrounded by impermeable rock, which forms a stratigraphic trap. Such oil pools are found in synclinal areas as well as anticlinal areas. The principal oil reservoirs are of Devonian age, roughly 50 to 100 million years older than the coal-bearing strata. The depth of the oil reservoirs is quite variable, but there is a general trend to increasing depth southwestward, in correspondence with the general structure of this part of the Appalachian Basin.

II.3.3 Natural Gas

Natural gas occurs in association with petroleum and with coal in Pennsylvania, as it does worldwide. There are also important gas pools in western Pennsylvania that are outside of the coal- and oil-producing areas, at least vertically (that is, by being deeper) if not areally. For example, oil is virtually absent from the eastern portion of the main bituminous coal field, but there is a major belt of gas reservoirs in that area; however, many of the gas reservoirs are deeper than the coal beds. As do the oilfields, the gas fields extend further north than the coal fields, but the distribution of gas is not the same as that of the oil. There are deep gas reservoirs in the northern tier of counties both to the east (as far as Tioga County) and to the west (to the Ohio border) of the main oil-producing belt. Some of the gas reservoirs are rocks of Silurian age, older than the important oil-producing sandstones. The Oil and Gas Map of Pennsylvania (1973) shows one gas field in Lackawanna County, in eastern Pennsylvania, close to part of the anthracite coal field, and some deep gas pools in Bedford County in the Appalachian Ridge and Valley Province.

Although coal is much more abundant in Pennsylvania than either oil or natural gas, gas occurs almost as widely (but not as continuously) across the state as does coal. In the vertical sense (and thus in the sense of geological age), gas is much more broadly distributed than is coal, with major occurrences in strata from Silurian age upward throughout the younger Paleozoic rocks.

III. AN EVALUATION OF POSSIBLE METHODS FOR RADIOMETRIC DATING OF COAL AND PETROLEUM

III.1 General Considerations

The insensitivity of nuclear decay constants to changes in physical and chemical conditions and the occurrence of a variety of radionuclides in most natural materials provide the basis for the radiometric dating methods, which have proved to be the only methods capable of providing accurate values for the absolute ages of materials over the whole range of geologic time. The radiometric dating methods may be classified in three groups:

1. Methods based on the decrease in abundance of a radionuclide from the time a material was formed to the present. Such a method requires measurement of the present amount of the radionuclide, and the original amount of the radionuclide must be established in some way. Radiocarbon dating is the best known and most widely used method in this category.
2. Methods based on the increase in amount of a daughter nuclide formed by decay of a radionuclide. In such a method, the present amounts of the parent and the daughter must be measured, and the initial amount of the daughter must be established in some way. The potassium-argon method is the most widely used method of this kind, but there are several other parent-daughter pairs that are of comparable importance in geochronology.

3. Methods based on the amount of radiation damage that has accumulated in a material. Such a method requires measurement of the amount of accumulated damage and a means of establishing the rate of accumulation of the radiation damage. Fission-track dating is the most widely used method of this kind.

Methods belonging to the first of these three categories may be applied to fluid materials as well as to solids, but methods in the second and third categories are generally applicable only to solids. Consequently, although there are a number of possible methods for radiometric dating of coal, the radiocarbon method is the only one that might reasonably be used to date oil and natural gas. Unfortunately, radiocarbon is relatively short-lived; materials older than 100,000 years will not have a measureable amount of ^{14}C remaining. Quite generally, the geological environments in which petroleum accumulations are found imply that the petroleum is much older than 100,000 years. The same is true for significant accumulations of natural gas, although there are some near-surface environments in which methane has formed in the recent past (and is being formed today). Radiocarbon dating is not useful for dating petroleum and major accumulations of natural gas because any radiocarbon that may once have been associated with these materials (or their precursors) has long since decayed away.

Coal cannot be dated by the radiocarbon method for the same reason the method is not applicable to petroleum. All known coal deposits are presumed to be much older than 100,000 years, and there is no evidence that radiocarbon is present in any coal. But since coal is a solid material, there are a number of other radiometric dating methods that might be used for dating coal deposits. In comparison to other kinds of rocks, very little consideration has been given to the possibility of dating coal by radiometric methods, because none of the

long-lived radionuclides that are so useful for dating silicate rocks is part of the essential constituents of coal. But these long-lived radionuclides are generally present as trace constituents of coal, either as part of the mineral impurities in the coal or as trace constituents of the substance of the coal itself.

Because of the great sensitivity of the methods currently used for isotopic measurement of radionuclides and their stable daughters, there is no doubt that techniques for accurate measurement of these trace constituents of coal could be devised. But there may be considerable doubt about the significance of such measurements, because of the heterogeneity and porosity of coal.

The long-lived radionuclides that are useful for dating rocks are isotopes of the metallic elements potassium, rubidium, samarium, thorium and uranium, elements that are present in the earth's crust primarily as constituents of silicate minerals. Silicate minerals are ubiquitous in coals, largely as the very fine-grained mateials known as clay minerals. In most if not all cases, there will be a considerably greater proportion of the long-lived radionuclides in the clay minerals than in the organic matter of coal. Unless an effective technique is developed to measure the amounts of a radionuclide and its daughter in the organic matter, separately from the larger amounts in the mineral matter, it is unlikely that useful information about the age of coal could be obtained by any radiometric dating method. The reason the mineral matter must be excluded from the measurements is that the minerals are generally detrital materials, which were formed in some other environment and transported to the site of deposition of the coal. Generally, such detrital material is considerably older than the coal that contains it, so the proportion of a radionuclide and its daughter in the detrital material is unrelated to the age of the coal. There may be an important exception to this

generalization, however. There is considerable evidence that clays may be altered during the formation of coal. If the degree of alteration of the clay is sufficiently great, then (some of) the clay minerals in or below a coal bed may in effect be new minerals having essentially the same age as the coal. In such a case, radiometric dating of the clay may be quite useful.

A major problem that may affect any attempt to directly date the organic matter of coal is the high degree of porosity of the material. Coals have intricate internal structures with a high percentage of very fine pores [Gan[29] and others]. Gas-adsorption studies have been used to show the nature of the porosity of coal and to gain information about the way in which the micropores are interconnected. The low density of coal and the high surface areas determined by the gas-adsorption studies suggest that coal is not likely to meet an essential criterion for radiometric dating based on the accumulation of a stable daughter nuclide, that is, that the material should have been a "closed system" in respect to the radionuclide and its daughter since the material formed. The problem may be particularly serious in cases where a daughter element is a gas, but ions of metallic elements may also migrate through coal since coal in place underground is usually saturated with water.

Following is an evaluation of each of the more commonly used radiometric methods of dating rocks in respect to its potential usefulness for dating coal.

III.2 The Potassium-Argon Method

The potassium-argon method is normally much more sensitive than the other radiometric dating methods, because the daughter element is an inert gas that is not normally incorporated into minerals when they are formed. The virtual absence of any of the daughter element initially means that the potassium-argon method may be useful for materials that contain very small amounts of

potassium. Dalrymple and Lanphere[30] gave a comprehensive description of the method, and their book is the best source of information on the principles of conventional potassium-argon dating. A variation of the potassium-argon method known as $^{40}Ar/^{39}Ar$ dating has come into common use since their book was published (see Dallmeyer[31]). In most applications, the $^{40}Ar/^{39}Ar$ technique can provide more useful information about the relation of potassium and argon than can conventional potassium-argon measurements.

The abundance of potassium in coals is more than sufficient for potassium-argon dating of the bulk material, but it is likely that nearly all of the potassium is part of mineral impurities rather than part of the coal. If, however, there is a small percentage of potassium in the organic material, then it is possible that potassium-argon measurements could be used to determine when the coal reached its present form (presumably some time after the actual deposition of the organic material).

For potassium-argon dating of coal to be successful, it is necessary that the coal has retained virtually all of the radiogenic argon that has formed within it, that any extraneous argon in the coal must have a definitive isotopic composition that would allow it to be distinguished from the radiogenic argon, that any such extraneous argon not be so abundant as to overwhelm the small amount of radiogenic argon that may be present, and that the potassium and argon in the organic part of the coal can be separated for measurement from potassium and argon in potassium-bearing minerals that are present in the coal.

The potassium-bearing minerals in coal, mostly clay minerals, are largely of detrital origin, which means that they would have already contained some radiogenic argon at the time they were incorporated into the coal. Such "inherited" radiogenic argon is related to materials and events that predate the coal, so the apparent potassium-argon age of the clay minerals within a

coal bed is likely to be greater than the age of the coal. But clay minerals are susceptible to alteration during and after their deposition in sedimentary layers, so one cannot make specific predictions about the apparent potassium-argon ages of sedimentary clays without some knowledge of the history of the rocks that contain them. Conversely, potassium-argon studies of clay minerals in sedimentary rocks of known age can provide a great deal of information about the history of the rocks [Sedivy and others[32]].

Recent work at Georgia Tech (not yet published) has shown that potassium-argon dating of rock salt having as little as 0.005% potassium is possible. This work was done by a new technique for potassium-argon dating, which takes advantage of the solubility of salt and the insolubility of silicate minerals in water. If a method could be found to release argon and potassium from the organic matter of coal without affecting the silicate minerals in the coal, then dating of coal may be possible even when there is very little potassium in the organic material. But the extent and nature of the porosity of coal may preclude satisfactory results. It is unlikely that the radiogenic argon formed within coal is quantitatively retained in the material, because of the opportunity provided by the network of micropores for such molecules to escape. The network of micropores also provides a path for extraneous argon to permeate the coal, and it may not be possible to get all such extraneous argon out of the coal before analysis. In this respect, coal is quite unlike rock salt, which appears to be essentially impermeable to argon. Unless virtually all of the atmospheric argon which permeates a coal sample can be removed in the laboratory, the K-Ar method would not have for coal the great sensitivity that makes it useful for dating rock salt of low potassium content.

An alternative approach would be to use the $^{40}Ar/^{39}Ar$ method, if the organic material releases argon under vacuum in a temperature range that is different from that at which the silicates release argon. [In the $^{40}Ar/^{39}Ar$ method some of the ^{39}K in a specimen is converted to ^{39}Ar by fast-neutron irradiation, and the amount of ^{39}Ar is then measured instead of measuring potassium directly. Since all of the isotopes of argon are released from a particular kind of material under the same conditions, potassium-argon apparent ages for different portions of a specimen may be obtained by releasing argon from the specimen in steps, usually by heating at progressively higher temperatures.) In principle, the information obtained by stepwise heating of material that has been irradiated for $^{40}Ar/^{39}Ar$ study can be used in favorable cases to get around the problem of atmospheric contamination and the problem of partial loss of the radiogenic argon within a material. But in a material with a thoroughly penetrative network of very fine pores, it is likely that recoil during formation of the ^{39}Ar will lead to considerable loss of ^{39}Ar from the material. Unless some domains exist in the coal that are impermeable to argon and at least one micrometer in diameter, it is not likely that $^{40}Ar/^{39}Ar$ studies of coal would be useful for dating. There is no reason to believe that such domains exist in the organic material of coal.

In summary, there appear to be some formidable problems in the application of potassium-argon dating to the organic material of coal, either by conventional methods or by the $^{40}Ar/^{39}Ar$ technique. On the other hand, the clay minerals in coal certainly can be dated by the potassium-argon technique, and if the process by which the coal formed had a sufficiently strong effect on the clay, either by causing chemical alteration or possibly by causing thermal alteration, then such dating of the clay should provide useful information about the origin of the coal.

III.3 The Rubidium-Strontium Method

^{87}Rb decays to ^{87}Sr with a half-life of about 49 billion years. Since rubidium is quite similar to potassium in its geochemical behavior, the Rb-Sr method is applicable to many of the materials for which potassium-argon dating is used. It has one great advantage over the K-Ar method: the daughter element is often retained in rocks under conditions of elevated temperature where argon will be lost. On the other hand, the fact that argon is a gas gives the K-Ar method a great advantage over the Rb-Sr method; in many cases the original amount of argon in a rock is nil, so the K-Ar method is generally much more sensitive than the Rb-Sr method. Strontium is always present as an original constituent of rubidium-bearing minerals and rocks, usually in sufficient quantity that the increase in ^{87}Sr content caused by decay of ^{87}Rb cannot be measured accurately unless the material is very old or relatively rich in rubidium. (For a similar reason, the decay of ^{40}K to ^{40}Ca is not used in radiometric dating. The K-Ca method is even much less sensitive than the Rb-Sr method.)

Like potassium, most of the rubidium in coal is presumably associated with the detrital minerals present in the coal. Consequently, Rb-Sr measurements on whole-rock samples of coal are not expected to provide useful information about the age of the coal (unless the detrital clay minerals were thoroughly altered during formation of he coal). As in the case of the K-Ar method, if a way could be found to measure the trace constituents of the organic matter in coal without any influence from the detrital minerals, then Rb-Sr measurements could perhaps provide information about the time when the coal formed. But because the rubidium content of the organic matter is likely to be extremely low, it is unlikely that the Rb-Sr method would be sufficiently sensitive in this application. The microporosity of coal is likely to be as severe a problem for

Rb-Sr dating of coal as it would be for K-Ar dating, since strontium is likely to be as mobile as (if not more mobile than) argon in water-saturated coal.

In summary, the possibility of dating coal by the rubidium-strontium method appears to be very slight, because the rubidium content of the organic material in coal is probably very low, because the separation of such trace metals in the organic material from what is present in detrital minerals is likely to be very difficult, and because the microporosity of the organic material makes it unlikely that the material has behaved as a closed system for rubidium and strontium. Although the same problems apply in the case of the potassium-argon method, the sensitivity of the K-Ar method is normally so much greater than that of the Rb-Sr method that any work done on coal for possible dating by these methods should first be focused on the K-Ar method.

III.3 The Samarium-Neodymium Method

^{147}Sm decays to ^{143}Nd with a half life of about 107 billion years. Because samarium and neodymium are both lanthanides, quite similar to one another in their chemical properties, the degree to which the two elements are separated from one another during geochemical processes is slight. For this reason and because of the smallness of the decay constant, the Sm-Nd relationship was not useful for dating rocks until the advent of methods for very high precision mass spectrometry of metallic elements in the late 1960's. After successful application to studies of meteorites in the early 1970's, Sm-Nd dating of terrestrial rocks began about a decade ago. The method has been quite useful for studies of many very old rocks that cannot be dated by other methods because of alteration of the rocks. The Sm-Nd relationship is much less sensitive to the effects of alteration than are the more commonly used parent-daughter pairs because of the geochemical character of the lanthanides. Like other Group III elements, these elements have very little

mobility in most natural fluids, so a small volume of rock may have behaved as a closed system in respect to these elements even though more mobile elements may have moved into or out of the rock.

It is probable that virtually all of the samarium and neodymium in coal is part of the detrital mineral impurities in the coal. Unless there were some way to effect an almost perfect separation of the organic matter from the mineral impurities, an analysis of samarium and neodymium would likely be dominated by the influence of the detrital minerals. Even if a perfect physical separation could be done, and even if there were enough Sm and Nd in the organic material for accurate measurement (neither of which is likely), the Sm-Nd method would not be favorable for dating coals. The method is best suited for rocks that are billions of years old, but all known coal deposits are within rocks that are less than half a billion years old.

III.4 The Uranium-Lead Method

Uranium has two characteristics, not shared by the other long-lived radioelements used in radiometric dating, that may in some cases allow it to be used for dating coal. First, uranium has two different oxidation states in the earth's crust. Under the reducing conditions that prevail in many environments where organic materials are abundant, uranium may be immobilized by reduction to U^{IV}. Consequently, uranium is sometimes highly enriched in materials that contain a lot of organic matter. Second, uranium has two long-lived isotopes, each of which decays via intermediates to a stable isotope of lead. This fortunate circumstance--two different parent-daughter pairs involving the same two elements--sometimes allows radiometric dating of uranium-bearing materials even if the materials have not been closed systems for uranium and lead.

The applicability of the uranium-lead method to organic-rich shales was evaluated by Cobb and Kulp[33]. They found evidence that some of the elements

in the uranium decay series as well as the stable lead isotopes formed in the last step of decay had moved within the porous rock, but they still were able to infer values for the ages of the rocks that have proved to be approximately correct. Since that time the uranium-lead method has been developed into a quite reliable method for dating certain minerals, particularly zircon, in spite of the fact that such minerals normally have lost some of their radiogenic lead. The theoretical basis for establishing the age of a material that has lost lead was first given by Wetherill[34].

Although uranium is commonly enriched in marine black shales, which form in anoxic environments, the uranium content of coal is not usually notably greater than that of ordinary rocks. Some coals have an enrichment of uranium, however, and there is considerable evidence that uranium is associated with the organic material in coal (Van der Flier and Fyfe[35]. Some of the uranium in coal must occur as a trace constituent of the detrital minerals, but in many cases a comparable or greater amount of uranium may be in the organic matter.

If uranium-lead dating of coal is to be successful, it will be necessary to find and isolate material that has a favorable ratio of uranium to original lead. Since lead is also sometimes enriched in rocks that formed in a reducing environment, because of its insolubility as the sulfide, it may be that most coals do not have a favorable ratio of uranium to lead. Perhaps, if the organic material of coal could be effectively separated from sulfide minerals as well as silicate minerals before analysis, the amount of original lead would not be a serious problem.

Because there are a series of energetic decay steps leading from uranium to lead and because of the porous nature of coal, it is unlikely that coal behaves as a closed system for uranium and lead or for some of the intermediate nuclides in the decay series. Nevertheless, there remains a possibility for

dating such open material if certain conditions have been met. Most important of these conditions is that lead should not have moved into the coal from the outside since the coal formed (but it is permissible for some of the radiogenic lead formed within the coal to have been lost to the outside). Another important condition is that there should not have been a severe loss of intermediates in the ^{238}U decay series. The most likely candidate for loss is the relatively long-lived ^{226}Ra.

In summary, uranium is the only one of the long-lived radioelements used for radiometric dating that might generally be more abundant in the organic matter of coal than in the mineral impurities in the coal. But the concentration of uranium in most coals is very low, and unless the content of ordinary lead is correspondingly low, uranium-lead dating of the material is not likely to be possible. Even in cases where coal may have a favorable ratio of uranium to lead, the porosity of the coal may have allowed continual movement of uranium, lead, and perhaps radium into and out of the coal to such an extent that U-Pb measurements will not provide useful information about the age of the coal.

As an example of U- and thorium-lead dating consider the following decay schemes:

1. U^{238} decays ultimately into Pb^{206} (stable)
   (See Table II.)
2. U^{235} decays ultimately into Pb^{207} (stable)
   (See Table III.)
3. Th^{232} decays ultimately into Pb^{208} (stable)
   (See Table IV.)

The differential equations governing the decay of U^{238}, U^{235}, and Th^{232} are respectively:

$$\frac{d\,N^{238}(t)}{dt} = -\lambda^{238}N^{238}(t); \quad \frac{d\,N^{235}(t)}{dt} = -\lambda^{235}N^{235}(t); \quad \frac{d\,N^{232}(t)}{dt} = \lambda^{232}N^{232}(t)$$

where N(t) is the number of atoms at time t
λ is the decay constant.

The solutions for these equations as a function of time is:

$$N^{238}(t) = N^{238}(o)e^{-\lambda^{238}t}; \quad N^{235}(t) = N^{235}(o)e^{-\lambda^{235}t} \text{ and}$$

$$N^{232}(t) = N^{232}(o)e^{-\lambda^{232}t}$$

For lead the following differential equations apply to U to Pb decay

$\frac{d\,Pb^{206}}{dt} = \lambda^{238}N^{238}(t) = \lambda^{238}N^{238}(o)e^{-\lambda^{238}t}$. The solution for this equation is

$$Pb^{206}(t) - Pb^{206}(o) = N^{238}(o)\left(1-e^{-\lambda^{238}t}\right)$$

Similarly for Pb^{207} the solution is:

$$Pb^{207}(t) - Pb^{207}(o) = N^{235}(o)\left(1-e^{\lambda^{235}t}\right)$$

and for Pb^{208} the solution is

$$Pb^{208}(t) - Pb^{208}(o) = N^{232}(o)\left(1-e^{-\lambda^{232}t}\right)$$

If we define the following

$$R_1 = U^{238}(o)/U^{235}(o)$$

$$R_2 = U^{238}(o)/Th^{232}(o)$$

$$R_3 = U^{235}(o)/Th^{232}(o) = R_2/R_1$$

and assume that $t = 4.5 \times 10^9$ years.

Then

$$\frac{Pb^{206}(t) - Pb^{206}(o)}{Pb^{207}(t) - Pb^{207}(o)} = 0.5055\ R_1$$

$$\frac{Pb^{206}(t) - Pb^{206}(o)}{Pb^{208}(t) - Pb^{208}(o)} = 2.5157\ R_2$$

$$\frac{Pb^{207}(t) - Pb^{207}(o)}{Pb^{208}(t) - Pb^{208}(o)} = 4.9763\ R_3$$

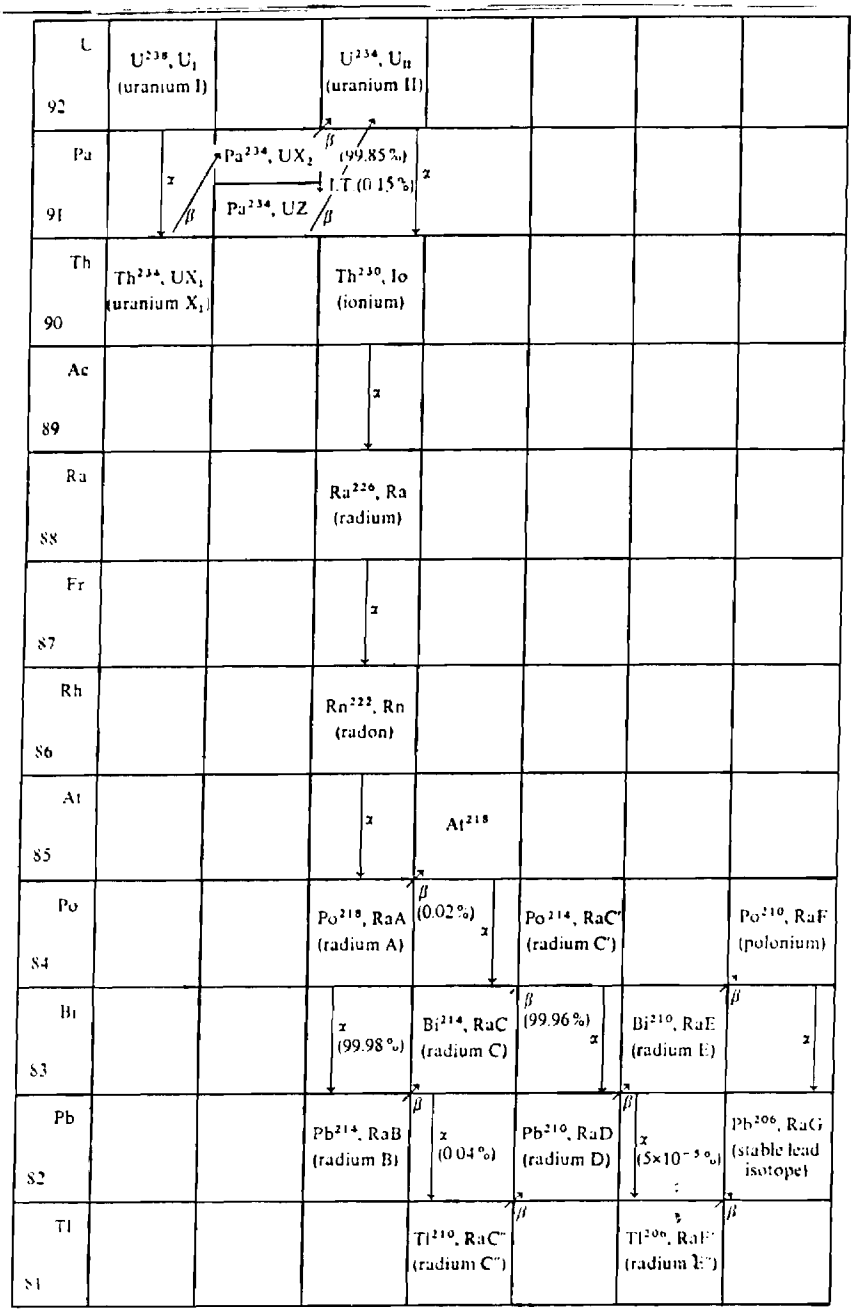
By trial and error one finds $R_1 = 1$

$R_3 = R_2 = 0.176149$ and $Pb^{206}(o) = 0.0277$

$Pb^{207}(o) = 0.0$ and $Pb^{208}(o) = 0.0277$

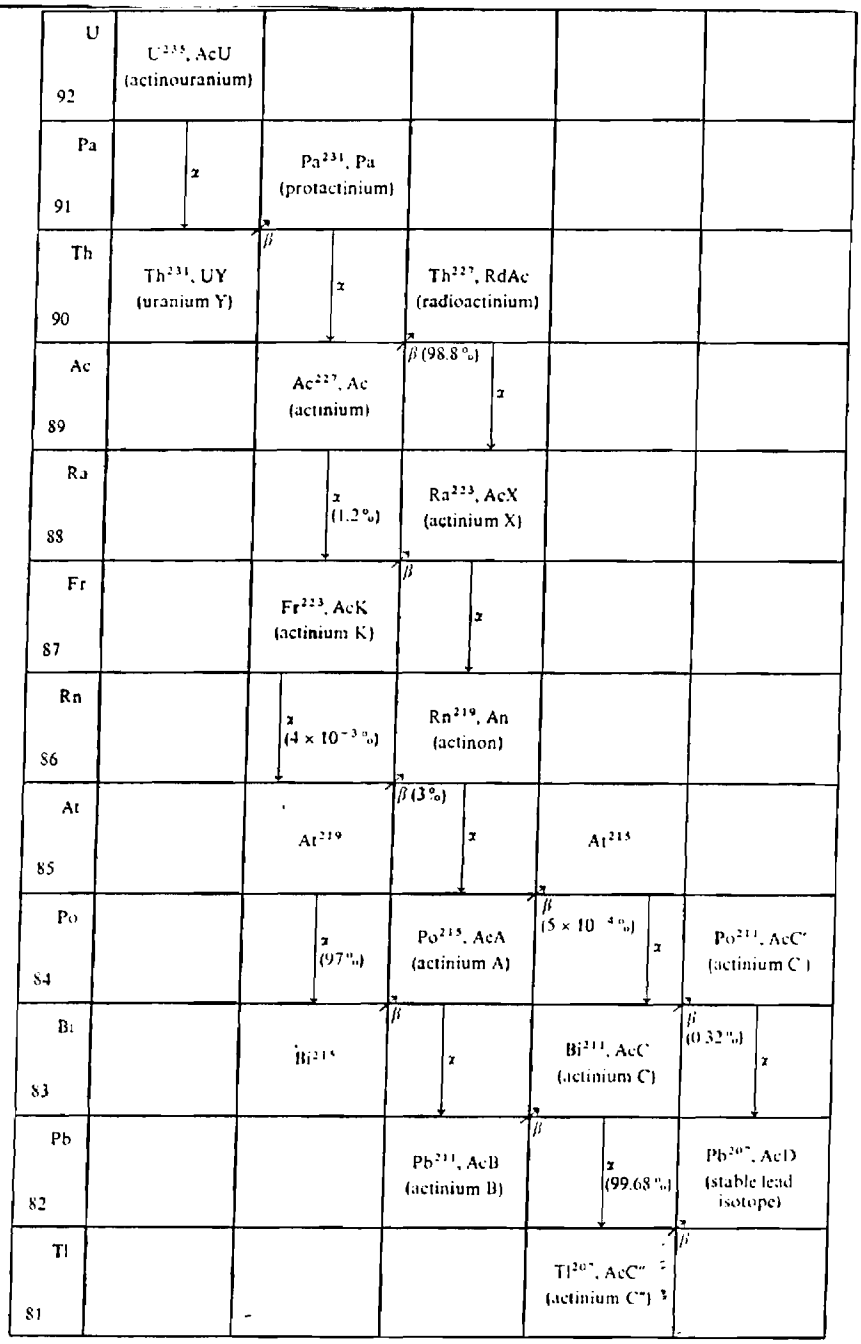
This suggests that by measuring in coal isotopic abundance of U^{238}, U^{235} and Th^{232} as well as Pb^{206}, Pb^{207} and Pb^{208}, it should be possible to date when these substances came together as coal.

TABLE 2. RADIOACTIVE DECAY SCHEME OF URANIUM-238 (1)*



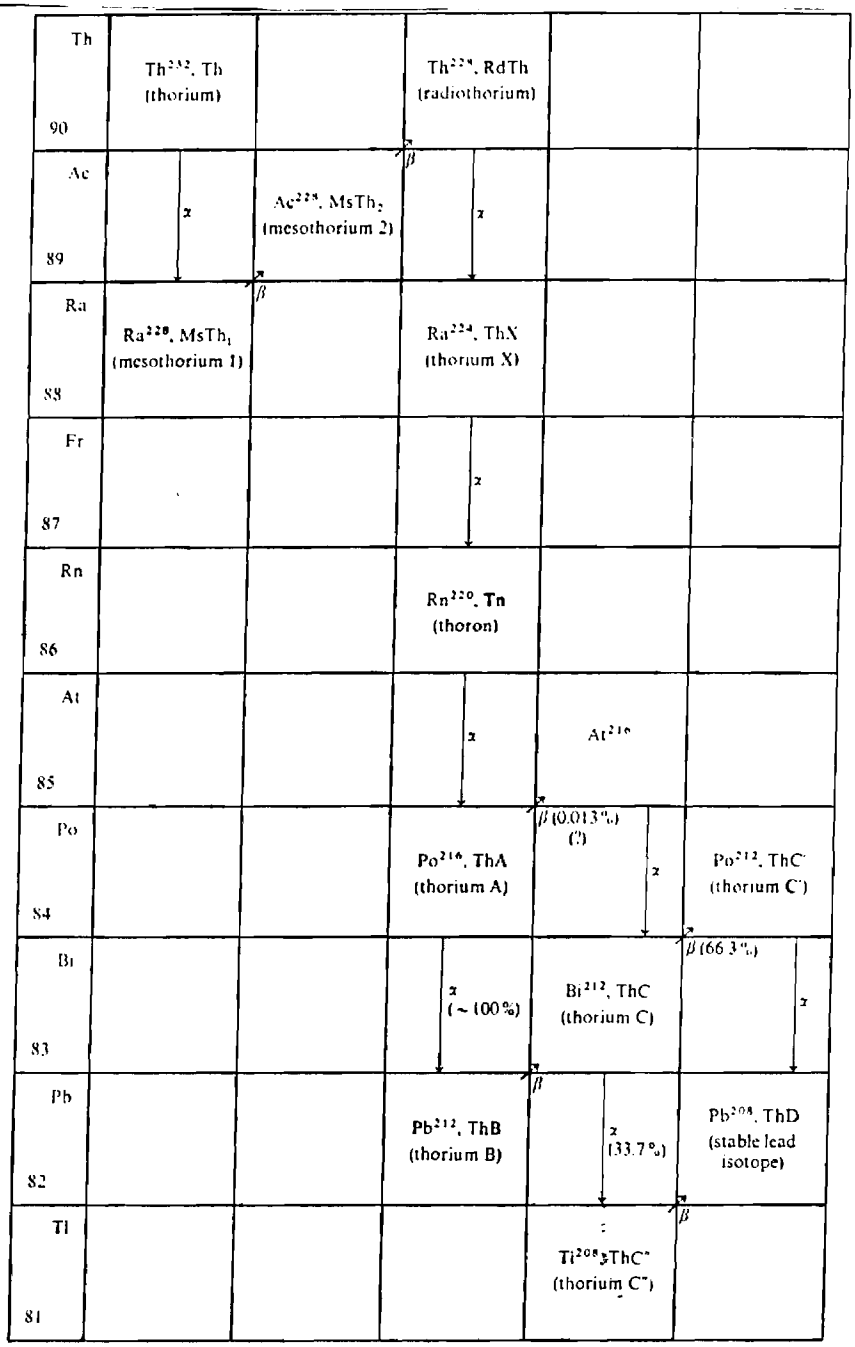
*For this reference see the list at the end of Additional Data Section.

TABLE 3. RADIOACTIVE DECAY SCHEME OF URANIUM-235 (1)*



*For this reference see the list at the end of Additional Data Section.

TABLE 4. RADIOACTIVE DECAY SCHEME OF THORIUM-232 (1)*



*For this reference see the list at the end of Additional Data Section.

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ADDITIONAL DATA

Table 1. Long lived Radioactive Nuclides

Parent	abundance* (%)	Daughter	abundance* (%)	Half-Life** (yr)	Type of Decay***
Potasium-40	0.01181	Argon-40	99.6	$1.3 * 10^9$	E.C.
		Calcium-40	99.97	(total)	Beta
Vanadium-50	0.24	Titanium-50	5.34	$\sim 6 * 10^{15}$	E.C.
		Chromium50	4.35	(total)	Beta
Rubidium-87	27.85	strontium-87	7.02	$4.7 * 10^{10}$	Beta
Indium-115	95.72	Tin-115	0.35	$5 * 10^{14}$	Beta
Tellerium-123	0.87	Antimony-123	42.75	$1.2 * 10^{13}$	E.C.
Lanthanum-138	0.0895	Barium-138	71.66	$1.1 * 10^{11}$	E.C
		Cerium-138	0.25	(total)	Beta
Neodymium-144	23.85	Cerium-140	88.48	$2.4 * 10^{15}$	Alpha
Samarium-147	14.9	Neodymium-143	12.17	$1.06 * 10^{11}$	Alpha
Hafnium-174	0.18	Ytterbium-170	3.03	$4.3 * 10^{15}$	Alpha
Lutetium-176	2.5	Hafnium-176	5.2	$2.2 * 10^{10}$	Beta
Rhenium-187	62.93	Osmium-187	1.64	$4 * 10^{10}$	Beta
Platinium-190	0.0127	Osmium-186	1.59	$7 * 10^{11}$	Alpha
Thorium-232	100.	Lead-208	52.3	$1.41 * 10^{10}$	6 Alpha + 4 Be
Uranium-235	0.7205	Lead-207	22.6	$7.13 * 10^8$	7 alpha + 4 Be
Uranium-238	99.274	Lead-206	23.6	$4.51 * 10^9$	8 alpha + 6 Be

*Reference (2)

**Reference (3)

***E.C electron capture

Table 2
RUBIDIUM CONTENT OF PLANT FOODSTFFS AND FODDERS (PPM DW) [4], [5], [6]

Plant	Tissue samples	Mean content
Cereal	Grains	4
Corn	Grains	3
Onion	Bulbs	1
Lettuce	Leaves	14
Cabbage	Leaves	12
Bean	Pods	51
Soybean	Seeds	220
Apple	Fruits	50
Avocado	Fruits	20
Clover	Tops	44
Lucerne (alfalfa)	Tops	98
Grass	Tops	130

Table 3
MEAN LEVELS AND RANGES OF STRONTIUM IN FOOD AND FEED PLANTS (PPM DW) [4], [7], [8] [9], [10], [11]

Plant	Tissue sample	Range	Mean
Wheat	Grains	0.48—2.3	1.5
Oats	Grains	1.8—3.2	2.5
	Green tops	9—31	20
Corn	Grains	0.06—0.4	—
Lettuce	Leaves	—	74
Spinach	Leaves	45—70	—
Cabbage	Leaves	1.2—150	45
Bean	Pods	1.5—67	18
Soybean	Leaves	58—89	—
Carrot	Roots	1.5—131	25
Onion	Bulbs	10—88	50
Potato	Tubers	—	2.6
Tomato	Fruits	0.4—91	9
Apple	Fruits	0.5—1.7	0.9
Orange	Fruits	—	0.5
Clover	Tops	95—850	219
Lucerne (alfalfa)	Tops	50—1500	662
Grass	Tops	6—37	24

Table 4
RUBIDIUM CONTENT OF SURFACE SOILS OF THE U.S. (PPM DW) [12]

Soil	Range	Mean
Sandy soils and lithosols on sandstones	<20—120	50
Light loamy soils	30—100	60
Loess and soils on silt deposits	45—100	75
Clay and clay-loamy soils	45—120	80
Alluvial soils	55—140	100
Soils over granites and gneisses	<20—210	120
Soils over volcanic rocks	20—115	65
Soils over limestones and calcareous rocks	50—100	75
Soils on glacial till and drift	30—80	66
Light desert soils	70—120	95
Silty prairie soils	50—100	65
Chernozems and dark prairie soils	55—115	80
Organic light soils	<20—70	30
Forest soils	<20—120	55

Table 5
STRONTIUM CONTENT OF SURFACE SOILS OF THE U.S. (PPM DW) [12]

Soil	Range	Mean
Sandy soils and lithosols on sandstones	5—1000	125
Light loamy soils	10—500	175
Loess and soils on silt deposits	20—1000	305
Clay and clay-loamy soils	15—300	120
Alluvial soils	50—700	295
Soils over granites and gneisses	50—1000	420
Soils over volcanic rocks	50—1000	445
Soils over limestones and calcareous rocks	15—1000	195
Soils on glacial till and drift	100—300	190
Light desert soils	70—2000	490
Silty prairie soils	70—500	215
Chernozems and dark prairie soils	70—500	170
Organic light soils	5—300	110
Forest soils	20—500	150
Various soils	7—1000	200

Table 6
STRONTIUM CONTENT OF SURFACE SOIL OF DIFFERENT COUNTRIES (PPM DW) [13]

Soil	Country	Range	Mean
Podzols and sandy soils	Australia	—	118
	New Zealand	350—570[a]	—
Loess and silty soils	New Zealand	220—380[a]	—
Loamy and clay soils	New Zealand	18—86[a]	—
	U.S.S.R.	280—310	295
Soils on glacial till	Denmark	—	14.7
Kastanozems	U.S.S.R.	—	280
Chernozems	U.S.S.R.	520—3500	—
Prairien and meadow soils	U.S.S.R.	150—500	300
Histosols and other organic soils	Denmark	—	92
Forest soils	U.S.S.R.	—	675
Various soils	Canada	30—500[b]	210
	Denmark	—	17.2
	Great Britain	—	261

[a] Soil derived from basalts and andesites.
[b] Data for whole soil profiles.

Table 7
INTERACTIONS BETWEEN MAJOR ELEMENTS AND TRACE ELEMENS IN PLANTS[4], [14], [15], [16]

Major element	Antagonistic elements	Synergistic elements
Ca	Al, B, Ba, Be, Cd, Co, Cr, Cs, Cu, F, Fe, Li, Mn, Ni, Pb, Sr, and Zn	Cu, Mn, and Zn
Mg	Al, Be, Ba, Cr, Mn, F, Zn, Ni[a], Co[a], Cu[a], and Fe[a]	Al and Zn
P	Al, As, B, Be, Cd, Cr, Cu, F, Fe, Hg, Mo, Mn, Ni, Pb, Rb, Se, Si, Sr, and Zn	Al, B, Cu, F, Fe, Mo, Mn, and Zn
K	Al, B, Hg, Cd, Cr, F, Mo, Mn, and Rb	—
S	As, Ba, Fe, Mo, Pb, and Se	Fe[b] and Fe
N	B, F, and Cu	B, Cu, Fe, and Mo
Cl	Br and I	—

[a] Reported for microorganisms.
[b] Mutual pollution causes significant injury.

Table 8

CONCENTRATION OF RARE EARTH ELEMENTS IN SOME U.S. COALS [17], [18]

Element	Illinois Basin			Eastern U.S.			Western U.S.		
	Range (ppm)	Arithmetic mean (ppm)	Geometric mean (ppm)	Range (ppm)	Arithmetic mean (ppm)	Geometric mean (ppm)	Range (ppm)	Arithmetic mean (ppm)	Geometric mean (ppm)
Cerium	4.4—46	14	12	11—42	25	23	2.8—30	11	9.1
Samarium	0.4—3.8	1.2	1.1	0.87—4.3	2.6	2.4	0.22—1.4	0.61	0.56
Europium	0.1—0.87	0.26	0.25	0.16—0.92	0.52	0.47	0.07—0.60	0.20	0.16
Terbium	0.04—0.65	0.22	0.18	0.06—0.63	0.34	0.28	0.06—0.58	0.21	0.17
Dysprosium	0.5—3.3	1.1	1.0	0.74—3.5	2.3	2.0	0.22—1.4	0.63	0.57
Ytterbium	0.27—0.15	0.56	0.53	0.18—1.4	0.83	0.73	0.13—0.78	0.38	0.34
Lutetium	0.02—0.44	0.09	0.08	0.04—0.40	0.22	0.18	0.01—0.43	0.07	0.05

Table 9
CONCENTRATION OF RARE EARTH ELEMENTS IN COAL (PPM) [17], [18]

Element	U.S. subbituminous	U.S. lignite	U.S. av	Worldwide av
Cerium (Ce)	5.5	12.3	7.7	11.5
Praseodymium (Pr)	6.1	2.7	2.7	2.2
Neodymium (Nd)	50	11	37	4.7
Samarium (Sm)	0.50	0.27	0.42	1.6
Europium (Eu)	0.61	0.13	0.45	0.7
Gadalinium (Gd)	0.13	0.21	0.17	1.6
Terbium (Tb)	0.1	0.1	0.1	0.3
Dysprosium (Dy)	2.7	1.4	2.2	—
Holmium (Ho)	0.13	0.06	0.11	0.3
Erbium (Er)	0.46	0.16	0.34	0.6
Thulium (Tm)	0.07	0.07	0.07	—
Ytterbium (Yb)	0.5	1.5	1	0.5
Lutetium (Lu)	0.09	0.05	0.08	0.07

TABLE 10

URANIUM-RADIUM (4n+2) SERIES (17)

Nuclide	Half-life	Type of decay and particle energies (MeV) (%)	Gamma energies — internal conversion (IC)
^{238}U	$4.51 \cdot 10^9$ years	α: 4.2 (100)	γ: 0.048 (0% + 23% IC)
^{234}Th	24.1 days	β^-: 0.19 (65), 0.10 (35)	γ: 0.091 (α_{IC} = 2.5), 0.063 (α_{IC} = 0.2), 0.029(α_{IC} = 10)
Protactinium-234 m	1.18 min	β^-: 2.31 (~90), 1.50 (~9), 0.58 (~1) IT: 1	1.00, 0.75, others
Protactinium-234	6.66 hr	β^-: 1.13 (13), 0.53 (27), 0.32 (32), 0.16 (28)	γ: 1.68, 1.43, 1.24, 0.924, 0.877, 0.803, 0.732, 0.603, 0.566, 0.368, 0.333, 0.293, 0.225, 0.153, 0.099, 0.043
^{234}U	$2.5 \cdot 10^5$ years	α: 4.768 (72), 4.717 (28)	γ: 0.051 0% + 28% IC)
^{230}Th	$8 \cdot 10^4$ years	α: 4.682 (76)	γ: 0.067 (0% + 24% IC)
^{226}Ra	1620 years	α: 4.777 (94.3)	γ: 0.188 (~4% + ~2% IC)
^{222}Rn	3.825 days	α: 5.48 (~100)	
^{218}Po	3.05 min	α: 6.00 (~100) β^-: (0.02)	
^{218}At	1.3 sec	α: 6.70 (~0.02), 6.65 (~0.001) β^-: (very weak)	
^{218}Rn	$1.9 \cdot 10^{-2}$ sec	α: 7.13 (very weak)	γ: 0.61 (very weak)
^{214}Pb	26.8 min	β^-: 0.65 (~44), 0.59 (~56)	γ: 0.35, 0.30, 0.24
^{214}Bi	19.9 min	α: ~5.5 (0.04), β^-: 3.26 (19), 1.88 (9), 1.51 (40), 1.0 (23), 0.4 (9)	: 1.76*, 1.12*, 0.61* others up to 2.43
^{214}Po	$1.6 \cdot 10^{-4}$ sec	α: 7.68 (~100)	
^{210}Ti	1.3 min	β^-: 0.061 (20), 0.015 (80)	γ: very weak
^{210}Pb	22y	β^-: 0.061 (20), 0.015 (80)	γ: 0.0465 (~5% + ~75% IC)
^{210}Bi	5.0 d	α: 5.06 ($1.7 \cdot 10^{-4}$) β^-: 1.17 (~100)	
^{210}Po	138.4 days	α: 5.305 (~100)	γ: 0.8 (very weak)
^{206}Ti	4.2 min	β^-: 1.51 ($1.7 \cdot 10^{-4}$)	
^{206}Pb	Stable		

* Most abundant.

TABLE 11

THORIUM SERIES (4n) (17)

Nuclide	Half-life	Type of decay and particle energies (MeV) (%)	Gamma energies — internal conversion (IC)
^{232}Th	$1.4 \cdot 10^{10}$ years	α: 4.007 (76), 3.948 (24) 3.948 (24)	γ: 0.059
^{228}Ra	6.7 years	β^- ~0.04 (100)	
^{228}Ac	6.13 hr	β^-: 2.10 (≅12), 1.76 (~12), 1.18 (~35), others of low energy (41)	γ: 0.057 to 1.46 (many lines)
^{228}Th	1.91 years	α: 5.421 (71), 5.338 (28) ~ 5.2 (0.4)	γ: 0.084 (2%), others (very weak)
^{224}Ra	3.64 days	α: 5.681 (95) 5.445 (4.9)	γ: 0.241 (3.2% + 0.5% (IC)
^{220}Rn	51.5 sec	α: 6.28 (~100)	
^{216}Po	0.16 sec	α: 6.775 (~100) β: 0.04	
^{216}At	3.10^{-4} sec	α: 7.79 (0.04)	
^{212}Pb	10.6 hr	β^-: 0.57 (~12), 0.33 (~80), others of low energy (8)	γ: 0.30 (~3%) + 1% IC), 0.24 (~36% + 36% IC), 0.12 (~0% + 3% IC)
^{212}Bi	60.5 min	α: 6.08 (10), 6.04 (25) others (1)	γ: 1.62, 1.08, 0.79, 0.73 (together ~ 10%) 0.04 (0% + ~ 25% IC) others weak)
		β^-: 2.25 (54), 1.52 (5), others of low energy (5)	
^{212}Po	$3 \cdot 10^{-7}$ sec	α: 8.78 (~64), others of higher energy (very weak)	
^{208}Tl	3.1 min	β^-: 1.79 (19), 1.52 (7), 1.25 (9), 1.03 (1)	γ: 2.62 (36%), 0.86 (4%) 0.58 (31%), 0.51 (~8% + ~ 1% IC), 0.28 (~3% + ~ 1% IC)
^{208}Pb	Stable		

TABLE 12

URANIUM-ACTINIUM SERIES (4n+3) (17)

Nuclide	Half-life	Type of decay and particle energies (MeV) (%)	Gamma energies — internal conversion (IC)
^{235}U	$7.1 \cdot 10^8$ years	α: 4.56 (7), 4.52 (4), 4.35 (84), 4.18 (6)	γ: ~0.2000 (>4%), 0.185 (55%), ~0.165, (>4%), 0.143 (12%), 0.110 (5%), 0.095 (9%)
^{231}Th	25.6 hr	β^-: 0.30, others	γ: 0.084, others
Protactinium-231	$3.4 \cdot 10^4$ years	α :5.046 (10), 5.017 (23), 5.001 (24), 4.938 (22), 4.722 (11), others	γ: 0.29, 0.027, many others
^{227}Ac	22 years	α: 4.94 (1.2) β^-: 0.046 (99)	
^{227}Th	18.2 days	α: 6.036 (23), 5.976 (24), 5.958 (3.5), 5.865 (3), 5.755 (21), 5.712 (5), 5.708 (8.7), 5.699 (4), others (~7.8)	γ: 0.24 (~10%), 0.05 (~7.5%), many others of low energy (weak), all highly converted
^{223}Fr	22 min	α: 5.34 (very weak) β^-: 1.15 (~1%)	γ: 0.31, 0.21, 0.08
^{223}Ra	11.7 days	α: 5.742 (10.5), 5.712 (50), 5.602 (24), 5.429 (2.4), others (13.1)	γ: 0.34 (2.8%), 0.32 (2.3%), 0.27 (10%), 0.15 (5.5%), 0.14 (4%), 0.12 (2%), all highly converted
^{219}Rn	3.9 sec	α: 6.818 (82), 6.547 (13), 6.419 (5)	γ: 0.40 (~5%), 0.27 (~9% + ~4% IC)
^{215}Po	$1.8 \cdot 10^{-3}$ sec	α: 7.360 (~100) β^-: (0.0005)	
^{215}At	$\sim 1 \cdot 10^{-4}$ sec	α: 8.00 (very weak)	
^{211}Pb	36 min	β^-: 1.39 (~80), 0.5 (~20)	γ: 0.83 (13%), 0.43 (6%), 0.40 (6%)
^{211}Bi	2.16 min	α: 6.617 (~83) 6.273 (17) β^-: 0.3%	γ: 0.35 (13% + 4% IC)
^{211}Po	0.52 sec	α: 7.44 (~0.3) 6.90 (weak), 6.57 (weak)	γ: 0.89 (weak) 0.57 (weak)
^{207}Tl	4.79 min	β^-: 1.44 (100)	
^{207}Pb	Stable		

TABLE 13

LEAD IN U.S. COALS (17)

Region	Coal	Conc range (ppm)	Arithmetic mean (ppm)	Geometric mean (ppm)
Appalachian	Bituminous	0.37—86	9.2	6.6
Interior province	Bituminous	0.78—590	44	18
N. Great Plains	Lignite	1.4—17	4.0	3.5
N. Great Plains	Subbituminous	0.72—58	5.5	4.1
Rocky Mountain	Subbituminous	0.95—76	8.0	6.0
Rocky Mountain	Bituminous	0.76—137	7.3	5.2
All U.S.	Different	0.06—1300	15	7.0
Illinois Basin	—	0.8—220	32	15
Eastern U.S.	—	1.0—18	5.9	4.7
Western U.S.	—	0.70—9.0	3.4	2.6
North Dakota	Lignite	1.5—8	5.44	

TABLE 14

LEAD CONTENT OF SURFACE SOILS OF THE U.S. (PPM DW) (13)

Soil	Range	Mean
Sandy soils and lithosols on sandstones	<10—70	17
Light loamy soils	<10—50	20
Loess and soils on silt deposits	10—30	19
Clay and clay loamy soils	10—70	22
Alluvial soils	10—30	18
Soils over granites and gneisses	10—50	21
Soils over volcanic rocks	10—70	20
Soils over limestones and calcareous rocks	10—50	22
Soils on glacial till and drift	10—30	17
Light desert soils	10—70	23
Silty prairie soils	10—30	21
Chernozems and dark prairie soils	10—70	19
Organic light soils	10—50	24
Forest soils	10—50	20
Various soils	<10—70	26

TABLE 15

LEAD CONTENT OF SURFACE SOILS OF DIFFERENT COUNTRIES (PPM DW) (13)

Soil	Country	Range	Mean
Podzols and sandy soils	Australia	—	57
	Canada	2.3—47.5	10.4
	Madagascar	—	37
	Poland	8.5—23.5	16
Loess and silty soils	Poland	14—32	26
Loamy and clay soils	Canada	1.5—50.1	16.6
	Chad	20—45	—
	Madagascar	—	48
	Poland	12.5—52	25
	U.S.S.R.	—	40
Soils on glacial till	Denmark	11.3—17.3	14.7
Fluvisols	Austria	16—22	19
	Great Britain	24—96	63
	Madagascar	19—47	—
	Poland	12.5—48.5	39
Paddy soils	Japan	6—189	29
Gleysols	Chad	20—50	—
	Poland	19.5—48.5	30
	U.S.S.R.	—	67
	Great Britain	17—63	40
Rendzinas	Ireland	25—45	—
	Madagascar	—	20
	Poland	17—46	28.5
Kastanozems and brown soils	Austria	13—31	21
	Great Britain	20—50	35
Ferralsols	Chad	10—30	—
	Sierra Leone	3—91	47
Chernozems	Poland	19—29	25
Prairien and meadow soils	U.S.S.R.	—	61
	West Germany	11.5—79.5	—
Histosols, other organic soils	Canada	1.5—50.0	12.6
	Denmark	43—176	50.5
	Great Britain	26—142	84
	Ireland	120	—
	Poland	18—85	—
Forest soils	China	—	26
	U.S.S.R.	10—56	37
Various soils	Austria	21—33	29
	Canada	—	20*
	Great Britain	15.5—41	29
	Japan	5—189	35
	West Germany	15—68	—

* Mean for whole profiles of arable soils.

TABLE 16

FORMS AND PRINCIPAL FUNCTIONS OF TRACE ELEMENTS THAT ARE ESSENTIAL FOR PLANTS (13)

Element	Constituent of	Involved in
Al*	—	Controlling colloidal properties in the cell, possible activation of some dehydrogenases and oxydases
As*	Phospholipid (in algae)	Metabolism of carbohydrates in algae and fungi
B	Phosphogluconates	Metabolism and transport of carbohydrates, flavonoid synthesis, nucleic acid synthesis, phosphate utilization, and polyphenol production
Br*	Bromophenols (in algae)	—
Co	Cobamide coenzyme	Symbiotic N_2 fixation, possibly also in non-nodulating plants, and valence changes stimulation synthesis of chlorophyll and proteins (?)
Cu	Various oxidases, plastocyanins, and ceniloplasmin	Oxidation, photosynthesis, protein and carbohydrate metabolism, possibly involved in symbiotic N_2 fixation, and valence changes
F*	Fluoracetate (in a few species)	Citrate conversions
Fe	Hemo-proteins and nonheme iron proteins, dehydrogenases, and ferrodoxins	Photosynthesis, N_2 fixation, and valence changes
I	Tyrosine and its derivatives (in angiosperms and algae)	—
Li*	—	Metabolism in halophytes
Mn	Many enzyme systems	Photoproduction of oxygen in chloroplasts and, indirectly, in NO_3 reduction
Mo	Nitrate reductase, nitrogenase, oxidases, and molybdoferredoxin	N_2 fixation, NO_3^- reduction, and valence changes
Ni	Enzyme urease (in *Canavalia* seeds)	Possibly in action of hydrogenase and translocation of N
Rb*	—	Function similar to that of K in some plants
Se*	Glycene reductase (in *Clostridium* cells)	—
Si	Structural components	—
Sr*	—	Function similar to that of Ca in some plants
Ti*	—	Possibly photosynthesis and N_2 fixation
V*	Porphyrins, hemoproteins	Lipid metabolism, photosynthesis (in green algae), and, possibly, in N_2 fixation
Zn	Anhydrases, dehydrogenases, proteinases, and peptidases	Carbohydrate and protein metabolism

* Elements known to be essential for some groups or species and whose general essentiality needs confirmation.

ADDITIONAL DATA

TABLE 17

METALS IN SURFACE SOILS AND EARTHWORMS (PPM) (13)

Metal	Soil	Earthworms	Ratio, worms/soil
Cd	2	15	7.5
	4	4	1
	1.6	11.1	6.9
	0.9	14.4	16
	1.1	18	16
	0.6	12	20
	0.1	2.7	27
	4.1	10.3[a]	27.6
Cu	20	13	0.65
	252	11	0.04
	335	11	0.03
	52	28	0.53
	26	18	0.69
	9	5	0.55
Hg	3.8	1.29[b]	0.33
	0.1	0.04[b]	0.40
Mn	1330	82	0.06
	226	28	0.12
	164	27	0.16
Ni	26	31	1.19
	18	29	1.61
	12	32	2.66
Pb	1314	3592	2.73
	629	9	0.01
	700	331	0.47
	94	101	1.04
	170	62	0.36
	20	9	0.45
	870[c]	109[c]	0.12
Zn	138	739	5.35
	992	676	0.68
	219	670	3.05
	49	400	8.16
	275	2000	7.27
	40	900	22.50
	81	662[a]	8.17

Note: Element concentrations expressed on dry weight basis. Organisms analyzed are *Lumbricus nibellus* or *L. terrestris*, except as indicated.

TABLE 18

THORIUM AND URANIUM IN MAJOR ROCK TYPES (PPM) (VALUES COMMONLY FOUND, BASED ON VARIOUS SOURCES) (13)

Rock type	Values commonly found	
	Th	U
Magmatic Rocks		
Ultramafic rocks Dunites, peridotites, pyroxenites	0.004—0.005	0.003—0.010
Mafic rocks Basalts, gabbros	1—4	0.3—1.0
Intermediate rocks Diorites, syenites	7—14	1.4—3.0
Acid rocks Granites, gneisses	10—23	2.5—6.0
Acid rocks (volcanic) Rhyolites, trachytes, dacites	15	5
Sedimentary rocks		
Argillaceous sediments	9.6—12.0	3—4
Shales	12	3.0—4.1
Sandstones	1.7—3.8	0.45—0.59
Limestones, dolomites	1.7—2.9	2.2—2.5

TABLE 19

THORIUM AND URANIUM CONTENTS OF SURFACE SOILS OF DIFFERENT COUNTRIES (PPM DW) (13)

Country	Th		U	
	Range	Mean	Range	Mean
Bulgaria	3.6—17.8	9.3	—	—
Canada	4.2—14.1	8.0	0.72—2.05	1.22
Great Britain	—	10.5	—	2.60
West Germany	0.4—15.0	8.0	0.42—11.02	—
India	—	—	—	11.00
Poland	1.4—7.2	3.4	0.10—2.33	0.79
U.S.	2.2—21.0	7.6	0.30—10.70	3.70

TABLE 20

URANIUM CONCENTRATIONS IN SOME U.S. COALS (17)

Region	Coal	Arithmetic mean (ppm)	Geometric mean (ppm)	Conc range (ppm)
Appalachian	Bituminous	1.6	1.2	0.10—19
Interior province	Bituminous	3.2	1.7	0.20—59
N. Great Plains	Lignite	1.6	1.2	0.21—13
N. Great Plains	Subbituminous	1.6	0.98	0.9—16
Rocky Mountain	Subbituminous	2.8	1.9	0.06—76
Rocky Mountain	Bituminous	2.0	1.4	0.13—42
All U.S.	Different	2.6	1.3	0.06—2700
Illinois Basin	—	1.5	1.3	0.31—4.6
Eastern U.S.	—	1.5	1.3	0.40—2.9
Western U.S.	—	1.2	0.99	0.30—2.5

TABLE 21

THORIUM CONCENTRATION IN SOME U.S. COALS (17)

Area	Conc range (ppm)	Arithmetic mean (ppm)	Geometric mean (ppm)
Western U.S.	0.62—5.7	2.3	1.8
Eastern U.S.	1.8—9.0	4.5	4.0
Illinois Basin	0.71—5.1	2.1	1.9

TABLE 22

ABUNDANCES (μg/g) OF THE CHEMICAL ELEMENTS (LISTED IN DECREASING CRUSTAL ABUNDANCE) (19)

Element	Crust	Granite	Basalt	Shale	Seawater
O	464,000	490,000	459,700	395,200	857,000
Si	282,000	323,000	240,000	238,000	3.0
Al	82,000	77,000	88,000	80,000	0.01
Fe	56,000	27,000	86,000	47,000	0.01
Ca	41,000	16,000	67,000	25,000	400
Na	24,000	28,000	19,000	6,600	10,500
Mg	23,000	1,600	45,000	13,400	1,350
K	21,000	33,000	8,300	23,000	380
Ti	5,700	2,300	9,000	4,500	0.001
H	1,400	400	600		108,000
P	1,050	700	1,400	770	0.07
Mn	1,000	400	1,500	850	0.002
Ba	600	1,200	180	580	0.03
F	500	700	250	500	1.3
S	260	270	250	220	885
Sr	215	250	180	450	8.0
C	200	300	100	1,000	28
V	180	16	240	130	0.002
Zr	155	210	100	200	
Cl	150	100	200	160	19,000
Rb	125	210	40	270	0.12
La	100	100	112	40	0.0000012
Ce	96	170	23	50	0.0000052
Ni	75	1	100	95	0.002
Cr	71	22	120	100	0.000005
Zn	70	45	82	80	0.01
Cu	60	13	110	57	0.003
Nd	36	55	17	23	0.0000092
Co	26	2	50	20	0.0001
Sc	20	3	34	10	0.00004
Y	19	13	25	23	0.0003
Li	18	24	12	60	0.17
Ga	17	18	16	19	0.00003
Nb	15	20	10	20	0.00001
N	15	10	20	60	0.5
Pb	14	20	5	20	0.00001
Th	10	17	2	11	0.00005
B	10	15	5	100	4.6
Pr	10	17	4	5	0.0000026
Sm	7	9	4	7	0.0000017
Gd	5	5	4	7	0.0000024
Hf	4	6	2	6	
Sn	4	4	3	6	0.0008
Dy	3	2	4	5	0.0000029
Er	3	2	3	3	0.0000024

TABLE 22 (CONTINUED)

Element	Crust	Granite	Basalt	Shale	Seawater
Mo	2	3	0.5	2	0.01
Yb	2	1.0	3	3	0.000002
U	2	3	0.50	3	0.003
Be	1.9	3	0.8	3	0.0000007
As	1.6	0.80	2	6	0.003
Ge	1.4	1.0	1.7	2	0.00006
Cs	1.3	1.5	1.0	5	0.0005
Eu	1.2	1.3	1.1	1.1	0.000000046
Ta	1.2	1.6	0.70	–	–
Ho	0.70	0.50	1.0	1.0	0.000000088
Sb	0.70	0.40	1.1	1.5	0.0005
Tb	0.70	0.60	0.80	0.90	–
Tl	0.70	1.3	0.13	1.0	<0.00001
W	0.40	0.40	0.45	2	0.0001
Tm	0.30	0.20	0.30	0.25	0.000000052
Lu	0.27	0.20	0.35	0.7	0.000000048
Br	0.26	0.13	0.40	6	65
Bi	0.20	0.10	0.25	0.01	0.00002
Cd	0.18	0.06	0.30	0.30	0.00011
Hg	0.17	0.24	0.11	0.40	0.00003
Se	0.10		0.11	0.60	0.0004
Ag	0.05	0.04	0.05	0.10	0.00004
I	0.05	0.05	0.05	1.00	0.06
In	0.05	0.025	0.07	0.05	<0.02
Pd	0.01	0.001	0.02	<0.05	<0.00001
Pt	0.01	0.001	0.02	<0.05	<0.00001
Te	0.01	0.01	0.01		
Au	0.005	0.005	0.005		0.00001
Rh	0.005	0.005	0.005	<0.05	<0.00001
Ir	0.001	0.006	0.00005	<0.05	<0.00001
Re	0.0005	0.0006	0.0004		
Os	0.0002	0.0001	0.0004	<0.05	<0.00001
Ru	0.0001	–	–	<0.05	<0.00001

$Pb^{206}_{(0)}$	$Pb^{207}_{(0)}$	$Pb^{208}_{(0)}$	$R_1 = \frac{U^{238}_{(0)}}{U^{235}_{(0)}}$	$R_2 = \frac{U^{238}_{(0)}}{Th^{232}_{(0)}}$	$R_3^{66} = R_2/R_1$ $\frac{U^{235}_{(0)}}{Th^{232}_{(0)}}$
0.141	0.01209	0.479	1.	1.	0.99667
0.0141	-0.2407?	?	1	?	?
0.0141	0.0141	0.15179	2.2462	0.25	0.1113
0.0141	0.0141	.2441	2.2462	1/3	0.14852
0.0141	-0.2349?	?	1.01276 (238/235)	?	?
0.0141	-0.011 ?	?	2.	?	?
0.1429	0.0141	0.35659	1	0.25	0.25
0.1429	0.0141	0.39769	1	1/3	1/3
0.03955	0.0141	0.192	2	0.25	0.125
0.03955	0.0141	0.2744	2	1/3	1/6
0.03955	0.0141	0.4388	2.	1	1/2
0.1429	0.0141	0.4387	1	1/2	1/2
0.	0.	0.	2.2281	0.1879	0.084
0.25295	0.	0.25295	2	0.177	0.17611
1.0277	0.	0.0277	1	0.176149	0.125
0.025295	0.	0.169599	2.	0.25	0.25
0.0277	0.	0.1734227	1.	0.25	1/3
0.0277	0.	0.257469	1.	1/3	

$U^{238} \longrightarrow Pb^{206}$ — 25.1 %, 25.2 %, 23.6 % } 24.63 % — $T_{1/2}^{238} = 4.51 \times 10^9$ yr

$\lambda_{238} = 1.5366 \times 10^{-10}$ yr^{-1}

$U^{235} \longrightarrow Pb^{207}$ — 21.7 %, 21.3 %, 22.6 % } 21.86 % — $T_{1/2}^{235} = 7.13 \times 10^8$ yr

$\lambda_{235} = 9.7195 \times 10^{-10}$ yr^{-1}

$Th^{222} \longrightarrow Pb^{208}$ — 52.3 %, 51.7 % } 52.1 % — $T_{1/2}^{232} = 1.41 \times 10^{10}$ yr

$\lambda_{232} = 4.9149 \times 10^{-11}$ yr^{-1}

$Pb^{204} \longrightarrow$ 1.4 %, 1.36 % } 1.41 %

[1]: $$\frac{Pb^{206}(t) - Pb^{206}(0)}{Pb^{207}(t) - Pb^{207}(0)} = \frac{U^{238}(0)}{U^{235}(0)} \frac{(1 - e^{-\lambda_{238} t})}{(1 - e^{-\lambda_{235} t})}$$

[2]: $$\frac{Pb^{206}(t) - Pb^{206}(0)}{Pb^{208}(t) - Pb^{208}(0)} = \frac{U^{238}(0)}{Th^{232}(0)} \frac{(1 - e^{-\lambda_{238} t})}{(1 - e^{-\lambda_{232} t})}$$

[3]: $$\frac{Pb^{207}(t) - Pb^{207}(0)}{Pb^{208}(t) - Pb^{208}(0)} = \frac{U^{235}(0)}{Th^{232}(0)} \cdot \frac{(1 - e^{-\lambda_{235} t})}{(1 - e^{-\lambda_{232} t})}$$

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